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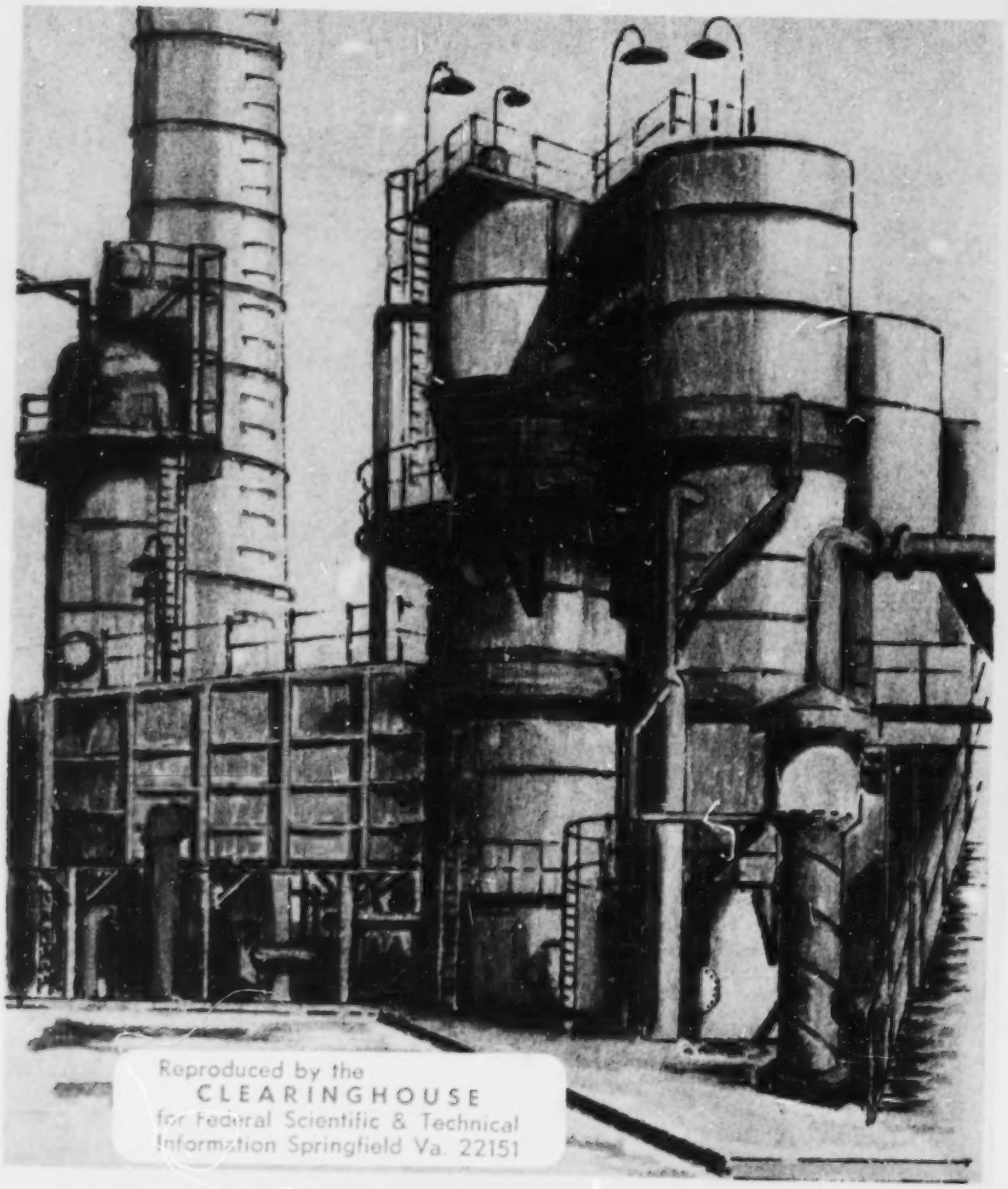
ATMOSPHERIC EMISSIONS FROM THERMAL-PROCESS PHOSPHORIC ACID MANUFACTURE



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U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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ATMOSPHERIC EMISSIONS FROM THERMAL-PROCESS PHOSPHORIC ACID MANUFACTURE

Cooperative Study Project

Manufacturing Chemists' Association, Inc.

and

Public Health Service

U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
Public Health Service
Consumer Protection and Environmental Health Service
National Air Pollution Control Administration
Durham, North Carolina
October 1968

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The AP series of reports is issued by the National Air Pollution Control Administration to report the results of scientific and engineering studies, and information of general interest in the field of air pollution. Information reported in this series includes coverage of NAPCA intramural activities and of cooperative studies conducted in conjunction with state and local agencies, research institutes, and industrial organizations. Copies of AP reports may be obtained upon request, as supplies permit, from the Office of Technical Information and Publications, National Air Pollution Control Administration, U.S. Department of Health, Education, and Welfare, Ballston Center Tower No. 2, 801 North Randolph Street, Arlington, Virginia 22203.

National Air Pollution Control Administration Publication No. AP-48

PREFACE

To provide reliable information on the nature and quantity of emissions to the atmosphere from chemical manufacturing, the Manufacturing Chemist's Association, Inc., and the National Center for Air Pollution Control, United States Public Health Service, Department of Health, Education, and Welfare, entered into a study agreement on October 29, 1962. A cooperative program was established to investigate emissions from selected chemical manufacturing processes and to publish information about them in a form helpful to air pollution control and planning agencies and to chemical industry management. Direction of these studies is vested in an MCA-USPHS Steering Committee, which is presently constituted of the following members:

Representing USPHS	Representing MCA
Stanley T. Cuffe*	Willard F. Bixby*
Robert L. Harris	Louis W. Roznoy
David Monti	Clifton R. Walbridge
Raymond Smith	Elmer P. Wheeler

Information included in this report describes the range of emissions during normal operating conditions and the performance of established methods and devices employed to limit or control these emissions. Interpretation of emission values in terms of ground-level concentrations and assessment of potential effects produced by the emissions are outside the scope of this program.

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*Principal representative.

ACKNOWLEDGMENTS

Many companies and individuals in the phosphoric acid industry have been helpful in promoting this study, and for their contributions, the project sponsors extend their sincere gratitude.

Special thanks is due the following companies for their participation in a program of stack sampling specifically for this study:

Hooker Chemical Corporation
The Tennessee Valley Authority
Monsanto Company
Stauffer Chemical Company

Don R. Goodwin, of the Public Health Service, and Fred G. Rolater, of Stauffer Chemical Company, were the investigators in the study and are the principal authors of this report. The sponsors acknowledge the services of the Stauffer Chemical Company in providing the services of Mr. Rolater.

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USE AND LIMITATIONS OF THIS REPORT

This report, one of a series concerning atmospheric emissions from chemical manufacturing processes,* has been prepared to provide information on phosphoric acid manufacture by the thermal process. This report does not include information on the manufacture of phosphoric acid by the wet process.

Background information is included to define the importance of the thermal-process phosphoric acid industry in the United States. Basic characteristics of the industry are discussed, including growth rate in recent years, uses for the product, and the number and location of the producing sites.

A process description is given for the thermal process. Process information includes discussion of normal process variables that affect the quantity of emissions, the normal range of emissions, and methods of controlling or reducing emissions. Supplemental material provides detailed emission sampling and analytical methods.

The emission and operating data in Table A-1 in Appendix A represent results from approximately 90 percent of the present number of establishments.**

Most of these data have been gathered from production records of phosphoric acid producers. The data also include results from several stack-sampling programs conducted during late 1966 and early 1967 by

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*Two previous reports have been published in this series: "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes," PHS Publ. No. 999-AP-13; and "Atmospheric Emissions from Nitric Acid Manufacturing Processes," PHS Publ. No. 999-AP-27. They are available from the Manufacturing Chemists' Association, Washington, D. C., and Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402.

**Establishment - a works having one or more thermal-process phosphoric acid plants or units, each of which is a complete production entity.

the United States Public Health Service. Results obtained from these tests are consistent with the data received from other industry sources.

Emissions to the atmosphere from a thermal-process phosphoric acid plant depend upon a number of factors, such as plant design, skill of operation, efficiency of hydration, and the type and operation of special devices to reduce emissions. This report should be reviewed in 5 to 10 years to determine whether revision is necessary to reflect prevailing conditions.

Although this report is an industry review primarily for public officials concerned with the control of air pollution, the information should also be helpful to chemical plant management and technical staffs concerned with the control of air pollution. It may also be helpful to engineering students, medical personnel, and other professional people interested in emissions from thermal-process phosphoric acid plants.

SUMMARY

PHOSPHORIC ACID PRODUCTION

Production of phosphoric acid by the thermal process has increased at an annual rate of about 8 percent during the period from 1953 to 1963, and this growth rate is expected to continue in the immediate future. Thermal-process acid is used primarily in the manufacture of industrial phosphates and generally has been confined to nonfertilizer use. In recent years high-purity thermal-process acid has been used in increasing quantities for the production of the new superphosphoric acids (up to 80 percent P_2O_5).[1]

At the present time 27 operating establishments, several of which have more than one furnace, produce more than 1,000,000 tons of phosphoric acid per year (P_2O_5 basis). Strength of acids produced varies from 75 to 85 percent phosphoric acid, although a few plants produce acid of up to 105 percent phosphoric acid.

EMISSIONS FROM THERMAL-PROCESS PHOSPHORIC ACID

The major atmospheric contaminant from thermal-process phosphoric acid manufacture is phosphoric acid mist discharged in the absorber exit gas. This gas stream also contains water vapor and trace amounts of nitrogen oxides. The concentration of acid mist from the plants that supplied data varies from 0.1 to 16.9 milligrams of acid mist (expressed as P_2O_5) per standard cubic foot of stack gas. Emission data are shown in Table A-1 in Appendix A.

A second important emission is the acid treating tank discharge gas, which can contain significant amounts of hydrogen sulfide. These emissions are intermittent and may range from 10 to 2500 parts per million of hydrogen sulfide, as shown in Table A-1.

CONTROL OF EMISSIONS

Operating practices have little effect on emissions of acid mist. Several abatement devices have the ability to reduce emissions of acid

mist by as much as 99.9 percent. Both high-pressure-differential wire-mesh mist eliminators and high-efficiency glass-fiber mist eliminators are capable of this high performance.

Emissions of hydrogen sulfide can be controlled by alkaline scrubbing or by incinerating the hydrogen sulfide in the phosphorus furnace.

EMISSION GUIDELINES

The emission and operating data in Table A-1 show that acid mist and spray can be controlled effectively by commercially available abatement devices. Collection efficiencies range from 95 to 99.9 percent, with about one-third of the collection efficiencies reported being 99.9 percent or better. This degree of control is possible in the production of 75 to 105 percent phosphoric acid.

Stack effluent from thermal-process phosphoric acid plants normally has a plume of from 50 to 100 percent opacity. The plume dissipates in a few hundred feet, depending on acid mist concentration and atmospheric conditions.

Since only trace amounts of nitrogen oxides are emitted from these plants, abatement equipment is not used to reduce these emissions.

Hydrogen sulfide emissions from the acid treating facilities are influenced by operating practices. The relatively small intermittent emissions of hydrogen sulfide can be controlled by alkaline scrubbing or can be oxidized in the phosphorus furnace to sulfur dioxide.

GROWTH OF PHOSPHORIC ACID INDUSTRY

In 1938 low-cost electric power became available in large quantities in the Tennessee River Valley. The availability of low-cost power and the presence of thermal-quality phosphate rock in the Maury County area of middle Tennessee brought about the production of elemental phosphorus by the electric furnace process. The thermal process of producing phosphoric acid was the natural outgrowth.

A very pure phosphoric acid can be produced by the thermal process. This acid normally is used to produce high-quality phosphates for food, drug, and detergent uses; and since 1940, production has increased at the same general rate as the demand for these products. A few installations now produce fertilizer-grade acid, but they account for only a small part of the annual production.

In 1941 the production of thermal-process acid was about 108,500 tons (P_2O_5 basis) while wet-process acid production was slightly higher at 132,000 tons. By 1945 production of thermal-process acid and wet-process acid were equal at about 132,000 tons each. Since 1945 both segments of the industry have continued to grow, but since 1950 wet-process acid production has exceeded thermal process production, as is shown in Figure 1. Production data are given in Table 1.

The thermal process is now used to produce approximately one-third of the phosphoric acid annually in the United States. The thermal-process acid industry can be expected to increase at the same rate as the national economy unless technical changes alter the cost differential between thermal and wet acid. Should thermal acid ever become economically attractive for fertilizer manufacture, production would increase rapidly.

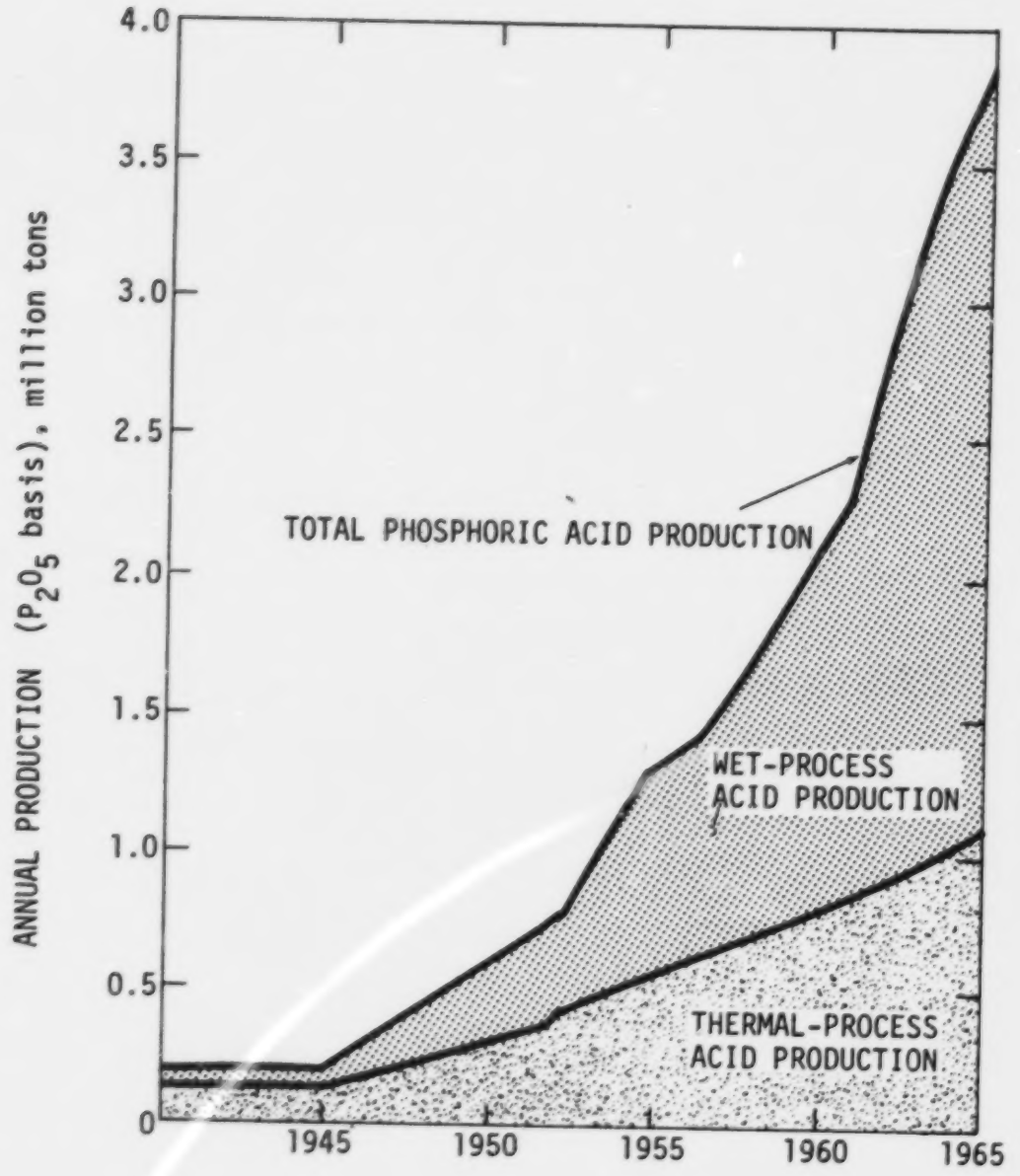

Figure 1. Production of phosphoric acid in United States, 1941 through 1965.

Table 1. GROWTH OF PHOSPHORIC ACID INDUSTRY IN UNITED STATES[2]

(tons/year 100% P_2O_5 basis)

Year	Thermal process	Wet process
1941	108,494	131,521
1942	104,655	118,970
1943	103,418	127,248
1944	111,157	141,141
1945	132,149	132,599
1947	191,911	174,987
1948	211,578	220,828
1949	259,677	245,427
1950	295,073	299,152
1951	330,096	338,426
1952	357,622	388,908
1953	462,580	496,152
1954	506,774	631,252
1955	540,025	774,998
1956	570,235	811,770
1957	632,954	936,129
1958	657,372	1,033,205
1959	740,747	1,140,658
1960	762,531	1,324,695
1961	844,761	1,409,173
1962	869,805	1,576,976
1963	947,293	1,957,476
1964	1,007,624	2,275,418
1965	1,007,941[a]	2,837,119

[a]Subject to revision.

THERMAL-PROCESS PHOSPHORIC ACID MANUFACTURE

INTRODUCTION

The process of producing phosphoric acid from elemental phosphorus is referred to by several names, including: the electric furnace process, phosphorus burning process, and thermal process. In this report it will be referred to as the thermal process.

Essentially all of the phosphoric acid produced in the United States is manufactured by either of two commercial processes. The wet process produces phosphoric acid from phosphate rock by treatment with sulfuric acid. The thermal process produces phosphoric acid by burning elemental phosphorus in air.

The cost of phosphorus pentoxide produced by the thermal process is nearly twice the cost of that produced by wet-process acid.[1] Thermal-process acid as normally produced contains 75 to 85 percent phosphoric acid (H_3PO_4), but a few plants produce an acid of 100 to 105 percent phosphoric acid. Acids of up to 115 percent phosphoric acid can be produced with modifications in process design and operation.

High-grade thermal-process phosphoric acid is normally used in the production of industrial phosphates, i.e., plasticizers, detergents, fire retardants, pharmaceuticals, and food-grade acid. Only a small quantity is used in the phosphate fertilizer industry.

RAW MATERIALS

Raw materials for the production of phosphoric acid by the thermal process are elemental (yellow) phosphorus, air, and water. Phosphorus is the basic raw material and is usually produced by the reduction of phosphate ore in electric furnaces. Phosphorus is normally handled in the molten state and must always be submerged under water or blanketed with inert gas because it ignites immediately when exposed to air. Phosphorus is usually produced at a point remote

from the thermal acid plant and is commonly shipped by rail as a liquid under water.

PROCESS DESCRIPTION

Thermal-process phosphoric acid manufacture, as shown in Figure 2, typically involves three steps.

1. Burning (oxidizing) the liquid elemental phosphorus in a suitable chamber to produce phosphorus pentoxide.
2. Hydrating the phosphorus pentoxide with dilute acid or water to produce phosphoric acid liquid and mist.
3. Removal of the phosphoric acid mist from the gas stream.

The following reactions are involved:

$$P_4 + 5\ O_2 \longrightarrow P_4O_{10}$$ (phosphorus pentoxide)

$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$$ (orthophosphoric acid, normally called phosphoric acid)

Phosphorus is transferred from the liquid phosphorus feed tank to the burner tower by a pump or by liquid displacement at feed rates that range from 1 to 5 gallons per minute. At the burner the phosphorus is mixed with air and is oxidized at temperatures of 3000° to 5000°F in the combustion chamber.[3] The resulting mixture of phosphorus pentoxide vapor and excess air passes from the combustion tower and into the hydrator.

Although many plants have refractory or graphite-lined combustion towers, a few new burning towers are constructed of water-jacketed stainless steel. In stainless steel towers weak phosphoric acid introduced into the combustion tower flows down the walls to remove excess heat. The phosphorus pentoxide vapors from the combustion tower are contacted with weak and product acid to hydrate the oxide to phosphoric acid and to absorb acid mist. This may be accomplished in one unit, but many plants use separate absorbing towers. In some new designs the acid sprayed into the hydrator is cooled prior to recycle. This permits use of a smaller quantity of acid and allows the

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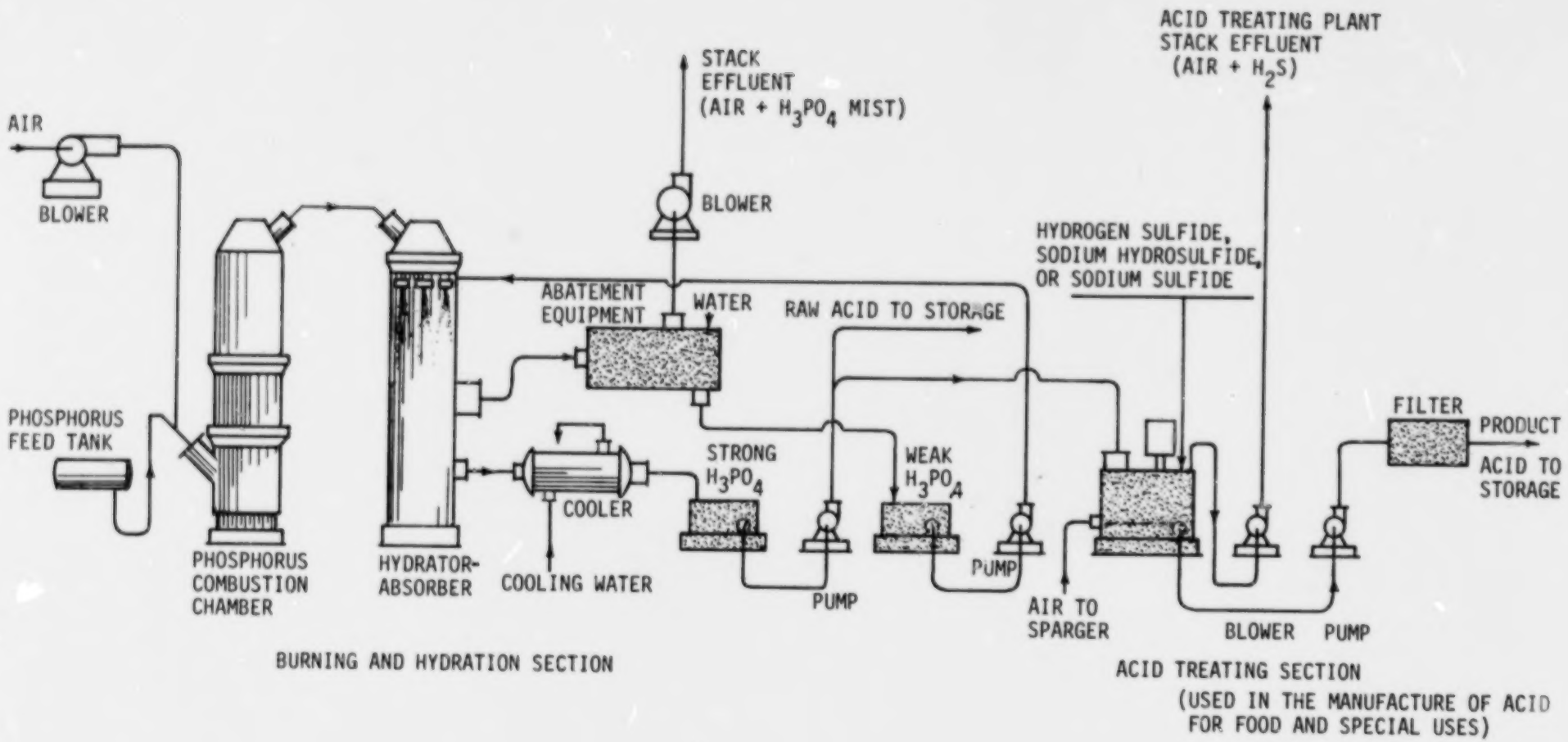


Figure 2. Flow diagram for typical thermal-process phosphoric acid plant.

production of higher strength acid.

Some product acid is drained from the bottom of the hydrator-absorber. Gases containing acid mist leave the hydrator-absorber and enter air pollution abatement equipment.

Venturi scrubbers, packed scrubbers, glass-fiber mist eliminators, wire-mesh mist eliminators, and electrostatic precipitators are used as abatement equipment at phosphoric acid plants. Weak acid collected in this equipment flows to storage tanks and is recycled within the process. Exhaust gas from the abatement equipment is discharged to the atmosphere.

Raw acid may contain arsenic, lead, and other heavy metals that make it unsuitable for use in food products. In the preparation of food-grade phosphoric acid the raw acid is treated with a sulfide to precipitate arsenic and other heavy metal ions. Hydrogen sulfide, sodium hydrosulfide, or sodium sulfide is added in excess of theoretical quantities to batches of raw acid to precipitate the metal sulfides. Sodium hydrosulfide is usually used. In the treating operation the solution is blown with air to remove excess hydrogen sulfide. The metal sulfides are removed from the acid by filtration before the product acid is transferred to storage.

YIELDS AND LOSSES

The yields from thermal production of phosphoric acid are exceptionally high. In efficient plants about 99.9 percent of the phosphorus burned is recovered as acid. The loss of acid through leaks and discharges to sewers is usually negligible. Losses of phosphoric acid to the atmosphere represent direct product loss; therefore, efficient collection devices are normally installed in the gas stream before the gas is discharged from the plant. The collector efficiency data given in Table A-1 show that the collector efficiencies range from 95.0 to 99.9 percent and average 98.0 percent. In most units, more than 90 percent of the acid is absorbed prior to the final collecting unit. Under these conditions, yields will approach 99.8 percent.

EMISSIONS FROM PHOSPHORIC ACID MANUFACTURE BY THERMAL PROCESS

PHOSPHORIC ACID MANUFACTURE

The principal atmospheric emission from the manufacture of phosphoric acid by the thermal process is acid mist in the absorber discharge gas. In the normal operation of the plants the hydration of phosphorus pentoxide (P_4O_{10}) creates phosphoric acid mist. Acid mist loadings within the process can be quite high. Loadings as high as 6000 milligrams per dry standard cubic foot of stack gas have been reported. It is not uncommon for as much as half of the total phosphorus pentoxide to be present as liquid phosphoric acid particles suspended in the gas stream.[4] Economical operation of the process depends on agglomeration of the acid mist particles and subsequent separation from the gas stream. For this reason all plants are equipped with some type of emission control equipment.

The gas stream from the hydrator contains phosphoric acid mist, often incorrectly referred to as P_2O_5 mist. Actually the acid mist is in the form of orthophosphoric acid (H_3PO_4). Unhydrated phosphorus pentoxide does not exist in stack gas.[4] The particle size of the acid mist ranges from 0.4 to 2.6 microns with a mass median diameter of 1.6 microns.[5] Figure 3 from Gillespie and Johnston[6] is a graph of particle-size distribution developed from laboratory experiments. Rough particle-size determinations made on three of the four plants sampled by the U.S. Public Health Service showed that 90 percent of the acid mist particles at the collector outlet were less than 5 microns in diameter.

The stack gas stream may contain as much as 60 percent and as little as 10 percent water vapor, depending on design and operating conditions. Water vapor in the plume usually ranges between 40 and 50 percent. This usually results in a dense white plume of 100 percent

opacity. Depending on weather conditions and acid mist concentration, the plume usually dissipates in a few hundred feet.

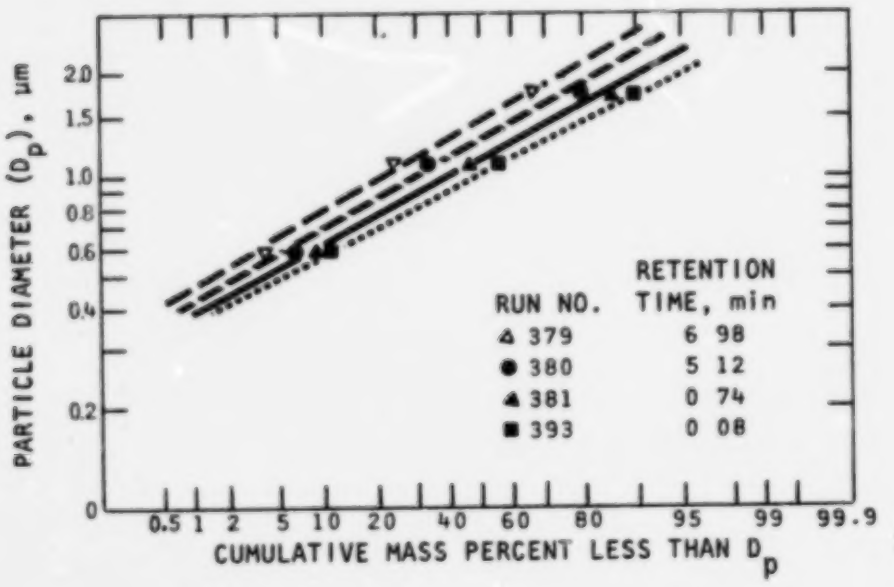


Figure 3. Particle size distribution of phosphoric acid mist. Mist loading, 1.0 mg/liter.

Table A-1 presents emission and operating data from 25 plants at which typical abatement equipment is used. Depending on plant operating conditions and type of abatement device, emissions range from 0.10 to 16.9 milligrams of phosphoric acid mist per standard cubic foot of stack gas (expressed as P_2O_5). The average emission of all plants supplying data and those that were sampled is 7.7 milligrams of phosphorus pentoxide per standard cubic foot of stack gas. The majority of the plants from which data are presented were producing 75 to 85 percent phosphoric acid and were operating within 10 percent of rated capacity.

Thermal-process acid manufacture employs high-temperature combustion that is normally conducive to the formation of nitrogen oxides. Many factors such as flame temperature, residence time, and quantity of excess air affect the amount of nitrogen oxides formed.

Because data on the quantity of nitrogen oxides formed in the thermal process is not generally available, two plants were sampled for nitrogen oxides. The data, listed in Table A-1, are from plants 12 and 24. The results, expressed as nitrogen dioxide, average 10 ppm. Apparently nitrogen oxide emissions are not significant in this process.

ACID TREATING

In the preparation of food-grade phosphoric acid the raw acid is treated with hydrogen sulfide, sodium hydrosulfide, or sodium sulfide. These chemicals are added in quantities slightly in excess of the theoretical amount. Heavy metals such as arsenic and lead are precipitated and separated by filtration. Excessive amounts of the treating chemical result in the formation of hydrogen sulfide, which is discharged from the treating tank. This emission is not continuous and may vary from substantial quantities for a short time to little, if any, detectable quantity.

Of the 25 plants that supplied data, 21 produce food-grade acid and, therefore, at times generate some hydrogen sulfide. Five plants reported hydrogen sulfide content of the acid-treater vent gas. The concentration of hydrogen sulfide in these plants ranged from 10 to 2500 parts per million.

OPERATING FACTORS AFFECTING EMISSIONS

No serious problems are encountered in the startup or shutdown of a thermal phosphoric acid manufacturing unit that affect losses from the final collector. Maintenance of proper liquid flows and pressure differentials on the absorbers and collectors allows little or no increase in acid mist discharged to the atmosphere during either startup or shutdown.

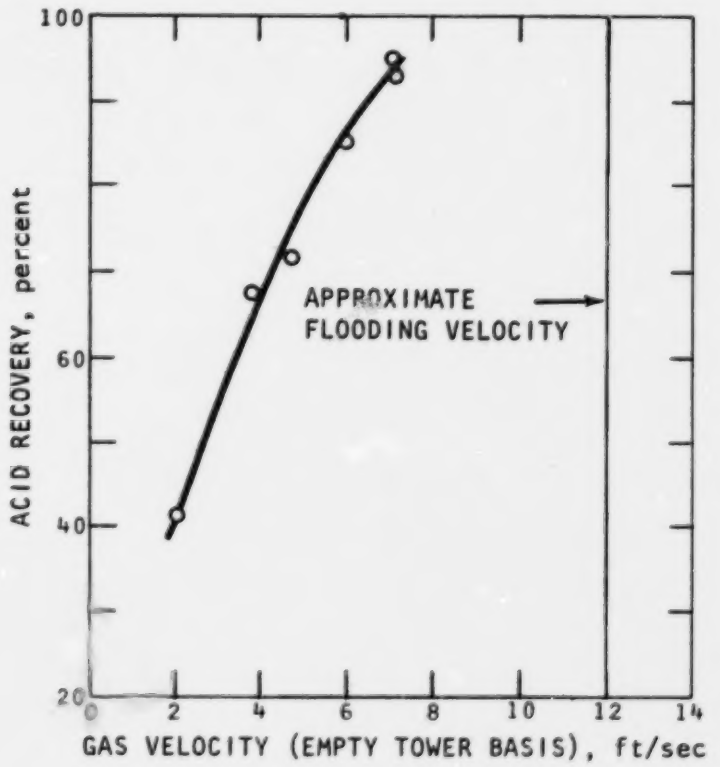
Maintenance is not usually considered to be a major problem. Sprays, fans, mist eliminators, and other equipment obviously must be maintained in good operating condition. If a continuous emission monitor is used on the collector exhaust, problems with the abatement equipment will be apparent to the operator quickly. Operators are normally concerned with keeping losses at a minimum because any loss is a direct loss of product.

ABATEMENT METHODS AND EQUIPMENT

Scrubbing

Packed and open tower scrubbers have been used widely to collect phosphoric acid mist. Low initial cost and ease of construction are advantages of these units. Conventional packing, e.g. Raschig rings or Beryl saddles, may be used. Both water and weak phosphoric acid are used as scrubbing media.

An important factor in efficient effluent collection for a given packed height is gas velocity. In one pilot plant study, collection efficiency increased from 40 to 95 percent while the gas velocity, calculated on the basis of an empty tower, increased from 2 to 7 feet per second.[7] This is shown in Figure 4.



TOWER PACKING - 18 ft OF 1-inch CARBON RASCHIG RINGS
ACID CONCENTRATIONS - 81-87% H_3PO_4
INLET GAS TEMPERATURE - 440°-550°F
P_2O_3 CONTENT OF GAS - 2.0-2.5 lb/1,000 ft^3

Figure 4. Effect of gas velocity on phosphoric acid recovery in pilot-plant packed tower.

Scrubbing is an inexpensive and simple abatement technique, but high collection efficiency is not usually obtained. Some plants have improved efficiency by installing wire-mesh mist eliminators after the scrubber.

Emission and operating data for plants that use such devices are presented (Plants 1 through 6, Table A-1). The emissions range from 3 to 14 milligrams P_2O_5 per standard cubic foot of stack gas. The average emission concentration from the six plants is 7.5 milligrams per standard cubic foot.

Venturi Scrubbers

Venturi scrubbers are capable of operating at high collection efficiencies on phosphoric acid mist. The extremely small size of the mist particles usually requires pressure differentials in excess of 40 inches of water. Collection efficiencies of venturi scrubbers are dependent on mist particle size, pressure drop across the venturi and spray liquid rate. The effect of particle size on efficiency is illustrated by Figure 5.[5] Collection efficiencies of 98 percent on 1-micron particles and 78 percent on 0.5-micron particles are reported.[5]

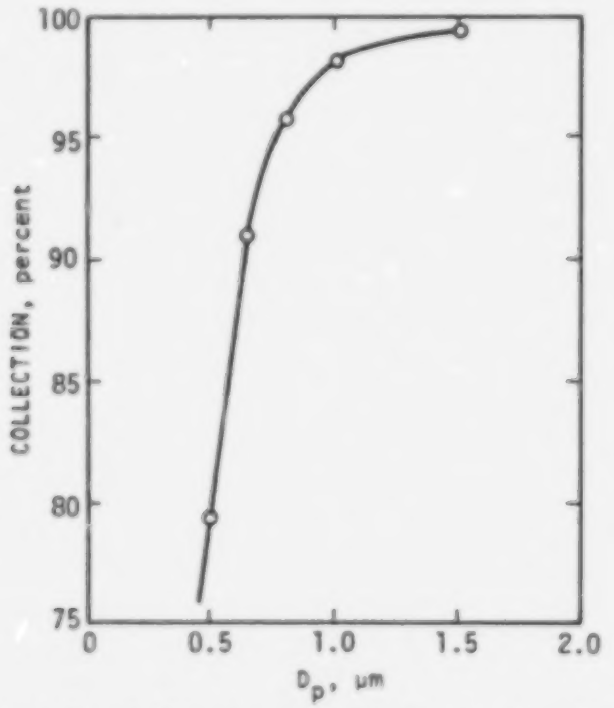


Figure 5. Collection efficiency of venturi scrubber as a function of particle size.[5]

Complete process data on a venturi gas scrubbing system are given in Table D-2.[3] Overall phosphorus pentoxide recoveries in excess of 99.9 percent are shown.

Plants 9 through 16 in Table A-1 provide operating and emission data of venturi scrubber installations. Acid mist concentrations vary from 6 to 17 milligrams of phosphorus pentoxide per standard cubic foot of stack gas.

Cyclonic Separators with Wire-Mesh Mist Eliminators

Cyclonic-type collectors are used in some plants to separate acid mist from hydrator-absorber effluent gas. Because of the small particle size of the acid mist other abatement devices usually supplement these collectors. Supplemental collectors are typically wire-mesh mist eliminator pads of low pressure differential. Data on two plants using this type of equipment are presented (Plants 7 and 8, Table A-1). Emission concentrations of 8 and 15 milligrams per standard cubic foot are given for these plants. High collector efficiency cannot be expected because cyclonic separators are not effective on particles of less than 10 microns in diameter.

In some plants venturi scrubbers are provided after the hydrator to operate in series with cyclonic separators. These venturi scrubbers have several functions and are not used solely for abatement. They actually hydrate part of the phosphorus pentoxide vapor, agglomerate the fine acid mist particles, and cool the stack gases. Up to half of the product acid may be recovered by the venturi - cyclonic separator system. Cool weak acid is added at the venturi throat. Gases are cooled rapidly by the evaporation of water from the acid and the expansion of the gas. A venturi scrubber followed by a cyclonic separator can recover up to 99.9 percent of the acid mist at pressure drops of 35 to 60 inches of water. In a system of this type the inlet loading to the venturi may be as high as 6000 milligrams of phosphorus pentoxide per standard cubic foot. Table A-1 shows data for this type of system (Plants 10, 11, 12, and 13). Emission concentrations range from 2.5 to 16.9 milligrams of phosphorus pentoxide per standard cubic foot of gas.

The average of the four plants is 10.6 milligrams of phosphorus pentoxide per standard cubic foot of stack gas.

Fiber Mist Eliminators

Glass fiber mist eliminators are capable of high collection efficiency in removing phosphoric acid mist from absorber effluent gas streams. Table 2 reports collection efficiencies of 95.2 to 99 percent with particles of less than 3 microns in size in pilot units using vapor velocities of 1.4 to 4.8 feet per second.[8] Table A-1 gives process and emission data for plants with glass fiber mist eliminators (Plants 17, 18, 19, 20, 21, and 22). These plants operated with collector efficiencies of 96 to 99.9 percent at gas velocities ranging from 0.4 to 13 feet per second. The pressure drop of these units varied from 7 to 22 inches of water. Emissions reported ranged from 0.1 to 9.0 milligrams of phosphorus pentoxide per cubic foot of stack gas. The average emission of this group of plants was 2.4 milligrams of phosphorus pentoxide per cubic foot, which is well below the average of 7.7 milligrams of phosphorus pentoxide per standard cubic foot for all plants reported in the study. When mist eliminators are operating at a superficial vapor velocity of less than 1 foot per second and at pressure differentials of about 20 inches of water, collection efficiencies of 99.9 percent are attainable. Plants 21 and 22, examples of this type of installation, report emissions of 0.1 and 0.25 milligram of phosphorus pentoxide per standard cubic foot of stack gas. Plants 21 and 22 also report clear stacks.

The stack gases leaving phosphoric acid plants can be made completely invisible when the mist loading is reduced to 0.02 milligram of phosphorus pentoxide per standard cubic foot of stack gas, the concentration of mist in the collector is at least 75 percent phosphoric acid, and the stack gas temperature is above 80°C. Under these conditions, the water vapor present in the gases disperses in the atmosphere before the gases are cooled below their dew point.[9]

Good gas distribution is mandatory for glass fiber mist eliminators.

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Table 2. PHOSPHORIC ACID MIST COLLECTION BY HIGH-EFFICIENCY FIBER MIST-ELIMINATOR PILOT UNIT AT HIGHER VELOCITIES[8]

Hours of operation	Flow through pilot unit, cfm	Flow through pilot unit, fps	Mist loading of gases into pilot unit,[a] mg P_2O_5/scf	Mist loading of gases from pilot unit, mg P_2O_5/scf	Collection efficiency on particles 3 microns and smaller, %
4	219	4.6	38.9	0.53	98.6
5	219	4.6	32.1	0.57	98.2
6	219	4.6	27.4	0.60	97.8
7	68	1.4	40.2	0.60	98.5
8	68	1.4	39.2	0.31	99.2
2,521	146	3.1	47.5	1.45	97.0
2,522	146	3.1	45.8	2.20	95.2
2,523	146	3.1	50.5	2.03	96.0
2,546	224	4.8	40.8	1.35	96.7
2,547	224	4.8	40.0	1.27	96.8
2,548	224	4.8	35.1	1.21	96.6
3,623	142	3.1	5.9	0.04	99.3
3,627	142	3.1	6.7	0.08	98.8
3,628	142	3.1	5.0	0.18	96.4
3,289	142	3.1	18.7	0.50	97.3
6,290	142	3.1	19.3	0.49	97.5
6,291	142	3.1	18.9	0.41	97.8

[a]The mist loading values given are for particles 3 microns and smaller in diameter.

High-Energy Wire-Mesh Contactors

The high-energy wire-mesh contactor is a recently developed abatement device, which is reported to give collection efficiencies that exceed 99.9 percent at pressure differentials ranging from 35 to 41 inches of water pressure drop.[10] Data on one installation are presented under plant 23, Table A-1. An emission concentration of 0.63 milligram of phosphorus pentoxide per standard cubic foot of stack gas is reported at a pressure drop of 39 inches of water. The unit has the advantage of operating at relatively high superficial vapor velocities of 20 to 30 feet per second, which results in low capital cost. One operating company is reported to have this type of scrubber installed on four of its plants.[11] Capital cost of wire-mesh mist eliminators is reported

to be approximately $1.50 per actual cubic foot per minute of stack gas.[10]

Electrostatic Precipitators

Electrostatic precipitators are highly efficient when used to collect acid mist regardless of the size of the acid mist particles.[12] Phosphorus pentoxide losses from electrostatic precipitators are affected only slightly by rate of gas flow or by temperature, as long as the design conditions are not exceeded. Acid mist losses are affected by the cleanliness of the equipment and the electrical conditions employed in its operation.[4] Precipitators operate at a pressure drop of about 0.5 inch of water. One source reports collection efficiencies of 98 to 99 percent when using electrostatic precipitators, but at high maintenance cost.[13] Data on plant 25 (Table A-1) show an emission concentration of 12 milligrams per standard cubic foot of stack gas. Table 3 shows electrostatic precipitator data from six installations.[14]

Table 3. OPERATING CHARACTERISTICS OF PHOSPHORIC ACID MIST ELECTROSTATIC PRECIPITATORS[14]

Installation	Gas flow rate[a], scfm	Inlet temperature, °F	Inlet mist conc. as noted	Outlet mist conc. as noted	Collector efficiency, %	Rated capacity, %
1	3,160	227	7.45[b]	0.08[b]	98.9	147
2	14,100	292	14.21[b]	0.415[b]	97.1	119
3	3,540	173	3468[c]	0.10[c]	99.9+	75
4	3,900	192	3650[c]	0.16[c]	99.9+	114
5	3,570	195	4060[c]	0.24[c]	99.9+	104
6	7,300	234	278[d]	10.43[d]	96.3	101

[a] 29.92 in. Hg and 32°F.

[b] Grains/scf dry gas as P_2O_5.

[c] Milligrams 80% H_3PO_4/cf dry gas at temperature.

[d] Milligrams mist/scf dry gas at 60°F as P_2O_5.

Hydrogen Sulfide Emission Abatement

Many plants make no attempt to remove hydrogen sulfide from the acid-treating-tank vent gas. This pollutant is vented directly to

the atmosphere, usually through short stacks in the roof of the treating building.

Hydrogen sulfide can be removed from the stack gases by combustion or absorption. An inexpensive method is to vent the acid-treater effluent gases to the phosphorus furnace and incinerate the hydrogen sulfide to sulfur dioxide. Suitable flame arrestors must be provided in this line. Plants 2 and 17 (Table A-1) report the use of this method.

Weak solutions of caustic soda or soda ash may be sprayed counter-current to the gas stream in packed towers to remove the hydrogen sulfide according to the following reactions:

$$Na_2CO_3 + H_2S \longrightarrow NaHCO_3 + NaHS$$

$$2\ NaOH + H_2S \longrightarrow Na_2S + H_2O$$

Of the 22 plants producing food-grade acid, Plants 11 and 25 (Table A-1) report the use of this method of abatement.

GLOSSARY OF TERMS

Abbreviation	
°C	Temperature, degrees centigrade
cc	Cubic centimeter
cfpm	Cubic feet per minute
ft	Foot (feet)
ft^2	Square feet
ft^3, cu ft	Cubic feet
fpm	Feet per minute
fps	Feet per second
°F	Temperature, degrees fahrenheit
gr	Grain
in. H_2O	Inches of water
lb	Pounds
lbs/hr	Pounds per hour
mg	Milligram
mg/scf	Milligram per standard cubic feet
mm	Millimeter
mscfm	1000 standard cubic feet per minute
NA	Data not available
ppm	Parts per million by volume
psig	Pounds per square inch gauge
scf	Standard cubic feet measured at 60°F and 760 mm HG
scfm	Standard cubic feet per minute
sp gr	Specific gravity
yr	Year

Chemical Symbols	
H_2S	Hydrogen sulfide
Hg	Mercury
H_2O	Water
HNO_3	Hydrochloric acid

HCl	Hydrochloric acid
H_3PO_4	Ortho phosphoric acid
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NaS	Sodium sulfide
NaHS	Sodium bisulfide
Na_2CO_3	Sodium carbonate
NO_x	Total nitrogen oxides in a mixture
NO	Nitric oxide
NO_2	Nitrogen dioxide
O_2	Oxygen
P_4	Phosphorus
P_2O_5, P_4O_{10}	Phosphorus pentoxide

Definitions

Contaminant	Any substance not normally present in the atmosphere.
Combustion tower	Refractory graphite-lined or water-jacketed stainless steel tower in which phosphorus is burned to phosphorus pentoxide.
Effluent	Waste gas stream that enters the atmosphere from the process.
Emission	Any gas stream emitted to the atmosphere.
Establishment	A works having one or more phosphoric acid plants or units, each of which is a complete production entity.
Food-grade acid	Phosphoric acid that has been treated for removal of heavy metals and is suitable for use in food products.
Hydrator-absorber	A single or double tower in which phosphorus pentoxide is hydrated to phosphoric acid and the resulting acid mist is absorbed.
Phosphoric acid mist	Extremely small particles of phosphoric acid that are true aerosols.

Phosphoric acid spray	Large phosphoric acid particles introduced into the gas by mechanical entrainment.
Raw acid	Impure phosphoric acid that contains heavy metallic impurities.

APPENDIX A: EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Most of the emission and operating data in Table A-1, which makes up Appendix A, were supplied by the manufacturers of phosphoric acid. Data from a variety of types and sizes of plants are included. The emission data are from 90 percent of the present thermal process establishments and include the results of the U.S. Public Health Service stack sampling program.

The table lists data from 25 separate thermal-process phosphoric acid manufacturing plants. Each plant is numbered; operating and emission data are listed vertically under the number of each plant.

Capacity of each plant, feed rate at rated capacity, hydrator discharge data, and acid treater discharge data are listed in the table.

Included as hydrator discharge data are type of collector used, gas flow rate, stack gas temperature, collector pressure drop, superficial gas velocity in collector, oxides of nitrogen contained in stack gas, acid mist emitted, phosphorus emitted, level of production during testing, plume opacity, and collector efficiency.

Acid treater discharge data includes that for type of collector, gas flow rate, stack gas temperature, amount of hydrogen sulfide in stack gas, and level of production during testing.

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Table A-1. EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Plant number	1	2	3	4	5
Rated capacity, tons/day	116 of 85% H_3PO_4	131.5 of 75% H_3PO_4	116 of 85% H_3PO_4	407 of 75% H_3PO_4	135 of 80% H_3PO_4
Feed rate at rated capacity phosphorus, lb/hr	2,590	2,600	2,600	8,640	2,870
Hydrator discharge data					
Type of collector	Packed tower	Packed tower	Packed tower and wire-mesh mist eliminator	Packed tower and wire-mesh mist eliminator	Scrubber plus wire-mesh mist eliminator
Gas flow rate (dry), scfm	6,900	7,870	6,940	21,600	9,740
Stack gas temperature, °F	176	189	175	180	176
Collector pressure drop, in. water	1	3.3	1.5	5	7
Superficial gas velocity in collector, fps	1.6	60	2	10	9
NO_x (as NO_2) in stack gas, ppm	NA	NA	NA	NA	NA
Acid mist to collector, mg P_2O_5/scf	NA	214	650	NA	NA
Acid mist from collector, mg P_2O_5/scf	3	9.7	4.5	14	5
Acid mist emitted, lb P_2O_5/hr	2.7	10.1	4.1	40.0	6.4
P_4 emission (% of P_4 burned)	0.057	0.169	0.069	0.252	0.097
Percent of rated capacity during sampling	90	100	100	80	100
Plume opacity	NA	100%	medium	medium	100%
Collector efficiency	NA	95.5	99.4	NA	NA
Acid treater discharge					
Type of collector	none	Piped to phosphorus burning tower	none	none	Food-grade not produced
Gas flow rate (dry), scfm	5,200	NA	870	NA	NA
Stack gas temperature, °F	176	NA	70	NA	NA
H_2S in stack gas, ppm	24 (maximum)	NA	10-20	NA	NA
Percent of rated capacity when sampled	100	NA	100	NA	NA

Table A-1 (continued). EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Plant number	6	7	8	9	10
Rated capacity, tons/day	162 of 87% H_3PO_4	179 of 85% H_3PO_4	189 of 80% H_3PO_4	110 of 75% H_3PO_4	217 of 105% H_3PO_4
Feed rate at rated capacity phosphorus, lb/hr	3,750	4,000	4,000	2,250	5,700
Hydrator discharge data					
Type of collector	Scrubber plus wire-mesh mist eliminator	Cyclonic separator wire-mesh mist eliminator	Cyclonic separator wire-mesh mist eliminator	Venturi plus wire-mesh mesh eliminator	Venturi, cyclonic separator and wire-mesh mist eliminator
Gas flow rate (dry), scfm	12,700	9,890	13,600	6,370	13,075
Stack gas temperature, °F	170	184	176	150	150
Collector pressure drop, in. water	3	8.5	8	0.5 (mist eliminator)	NA
Superficial gas velocity in collector, fps	9	9.5	10	280 (venturi)	NA
NO_x (as NO_2) in stack gas, ppm	NA	NA	NA	NA	NA
Acid mist to collector, mg P_2O_5/scf	NA	NA	NA	NA	NA
Acid mist from collector, mg P_2O_5/scf	9	15	8	16.3	6.5
Acid mist emitted, lb P_2O_5/hr	15.1	19.6	14.4	13.7	11.2
P_4 emission (% of P_4 burned)	0.151	0.246	0.157	0.302	0.086
Percent of rated capacity during sampling	116	87	100	88	NA
Plume opacity	medium	medium	100%	100%	NA
Collector efffciency	NA	NA	NA	NA	NA
Acid treater discharge					
Type of collector	none	none	none	none	Food-grade acid not produced
Gas flow rate (dry), scfm	NA	NA	NA	NA	NA
Stack gas temperature, °F	NA	NA	NA	NA	NA
H_2S in stack gas, ppm	NA	NA	NA	NA	NA
Percent of rated capacity when sampled	NA	NA	NA	NA	NA

Table A-1 (continued). EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Plant number	11	12	13	14	15
Rated capacity, tons/day	100 of 75% H_3PO_4	165 of 87.5% H_3PO_4	217 of 105% H_3PO_4	270 of 75% H_3PO_4	350 of 75% H_3PO_4
Feed rate at rated capacity phosphorus, lb/hr	2,000	3,950	6,000	5,300	7,000
Hydrator discharge data					
Type of collector	Venturi, cyclonic separator, wire-mesh mist eliminator	Venturi, cyclonic separator, wire-mesh mist eliminator	Venturi, cyclonic separator, wire-mesh mist eliminator	Venturi scrubber	Venturi scrubber
Gas flow rate (dry), scfm	4,900	7,460	6,922	6,600	15,500
Stack gas temperature, °F	175	175	142	201	168
Collector pressure drop, in. water	(excluding 6 venturi)	2.3 (excluding venturi)	52 (venturi) 22 (separator)	33	34
Superficial gas velocity in collector, fps	NA	-	201 (venturi) 5.9 (separator)	360	400
NO_x (as NO_2) in stack gas, ppm	NA	9.5	NA	NA	NA
Acid mist to collector, mg P_2O_5/scf	NA	-	5,989	625	NA
Acid mist from collector, mg P_2O_5/scf	2.5	16.9	6.7	15	9
Acid mist emitted, lb P_2O_5/hr	1.6	16.7	6.1	13.1	18.5
P_4 emission (% of P_4 burned)	0.037	0.185	0.048	0.108	0.121
Percent of rated capacity during sampling	95	100	91.5	100	95
Plume opacity	100%	100%	light	100%	medium
Collector efficiency	NA	NA	99.95	97.5	NA
Acid treater discharge					
Type of collector	Company design	none	Food-grade acid not produced	none	none
Gas flow rate (dry), scfm	NA	NA	-	107	NA
Stack gas temperature, °F	NA	NA	-	174	NA
H_2S in stack gas, ppm	NA	NA	-	2,500	NA
Percent of rated capacity when sampled	NA	NA	-	100	NA

Table A-1 (continued.) EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Plant number	16	17	18	19	20
Rated capacity, tons/day	151 of 100% H_3PO_4	120 of 75% H_3PO_4	200 of 75% H_3PO_4	60 of 75% H_3PO_4	250 of 75% H_3PO_4
Feed rate at rated capacity phosphorus, lb/hr	4,000	2,600	4,033	1,500	5,000
Hydrator discharge data					
Type of collector	Venturi scrubber	Glass fiber mist eliminator	Glass fiber mist eliminator	Glass fiber mist eliminator	Glass fiber mist eliminator
Gas flow rate (dry), scfm	17,775	5,000	6,140	3,440	17,000
Stack gas temperature, °F	165	185	180	136	170
Collector pressure drop, in. water	60	7.5	22	9	7
Superficial gas velocity in collector, fps	NA	0.92	13	0.4	7
NO_x (as NO_2) in stack gas, ppm	NA	NA	NA	NA	NA
Acid mist to collector, mg P_2O_5/scf	NA	515	252	109	100
Acid mist from collector, mg P_2O_5/scf	6	3.5	9	2	3
Acid mist emitted, lb P_2O_5/hr	14.1	2.3	7.3	0.9	6.7
P_4 emission (% of P_4 burned)	0.192	0.039	0.079	0.027	0.065
Percent of rated capacity during sampling	80	NA	100	98	90
Plume opacity	100%	light	medium	light	light
Collector efficiency	NA	99.2	96	98.1	97
Acid treater discharge					
Type of collector	Food-grade acid produced	Piped to phosphorus burning tower	Wire-mesh mist eliminators	none	Food-grade acid produced
Gas flow rate (dry), scfm		NA	500	NA	-
Stack gas temperature, °F		NA	145	NA	-
H_2S in stack gas, ppm		NA	55 (calculated)	NA	-
Percent of rated capacity when sampled		NA	100	NA	-

Table A-1 (continued). EMISSION AND OPERATING DATA FOR THERMAL-PROCESS PHOSPHORIC ACID PLANTS

Plant number	21	22	23	24	25
Rated capacity, tons/day	504 of 77% H_3PO_4	NA (79% H_3PO_4)	405 of 75% H_3PO_4	100 of 90% H_3PO_4	150 of 75% H_3PO_4
Feed rate at rated capacity phosphorus, lb/hr	11 000	11,100	8,000	2,270	3,000
Hydrator discharge data Type of collector	Glass fiber mist eliminator	Glass fiber mist eliminator	High Δ P wire-mesh mist eliminator	Wire-mesh mist eliminator	2 electrostatic precipitators in series
Gas flow rate (dry), scfm	30,200	19,433	12,250	8,690	3,600
Stack gas temperature, °F	165	182	172	175	117
Collector pressure drop, in. water	18	21.5	39	NA	11
Superficial gas velocity in collector, fps	0.4	0.4	27	4	6.8
NO_x (as NO_2) in stack gas, ppm	NA	NA	NA	10	NA
Acid mist to collector, mg P_2O_5/scf	1,300	1,543	2,670	235	NA
Acid mist from collector, mg P_2O_5/scf	0.1	0.25	0.63	12.4	12
Acid mist emitted, lb P_2O_5/hr	0.40	0.65	1.0	14.2	5.7
P_4 emission (% of P_4 burned)	0.002	0.003	0.005	0.273	0.083
Percent of rated capacity during sampling	100	100	99.5	100	100
Plume opacity	0%	0%	100%	100%	light
Collector efficiency	99.9	99.9	99.9	95	NA
Acid treater discharge Type of collector	none	none	none	none	Packed tower
Gas flow rate (dry), scfm	1,000	NA	NA	NA	247
Stack gas temperature, °F	100	NA	NA	NA	94
H_2S in stack gas, ppm	NA	NA	NA	NA	218
Percent of rated capacity when sampled	NA	NA	NA	NA	100

APPENDIX B: SAMPLING AND ANALYTICAL TECHNIQUES

The sampling and analytical techniques described are those used by the Public Health Service to conduct source tests on four thermal-process phosphoric acid plants in this study. The analytical procedures are based on methods described in the literature and by manufacturers of phosphoric acid.

DETERMINATION OF PHOSPHORIC ACID MIST

Description of Sampling Equipment

The equipment used for sampling phosphoric acid mist is an adaptation of the particulate sampling train designed by the U. S. Public Health Service. The design of the sampling train is based on flexibility, portability, and ease of operation. The Public Health Service sampling train permits separation of the acid mist particulate into two fractions having particle diameters greater and less than 5 microns.

The sampling train is shown schematically in Figure B-1 and as it actually appears in Figures B-2 and B-3. The sampling train consists of a probe, cyclone, filter, four Greenburg-Smith impingers, pump, dry gas meter, calibrated orifice, and manometer.

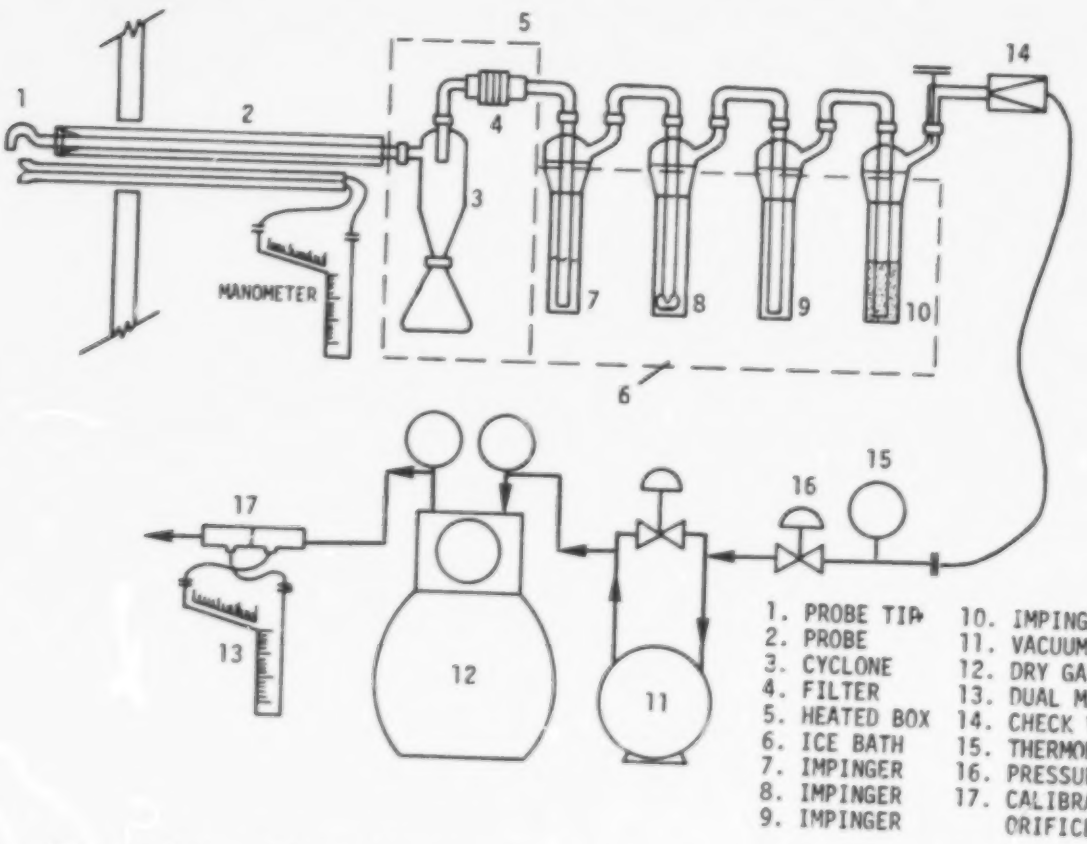


Figure B-1. Flow diagram of phosphoric acid mist sampling train.

The probe tip (1), a stainless steel button-hook type, is shown in Figure B-1. The probe (2) is made of 5/8-inch-diameter medium-wall Pyrex glass tube and is wound with 25 feet of 26-gauge nickel-chromium alloy wire to heat the probe during sampling. A variable transformer controls the temperature of the probe. To protect the glass probe the

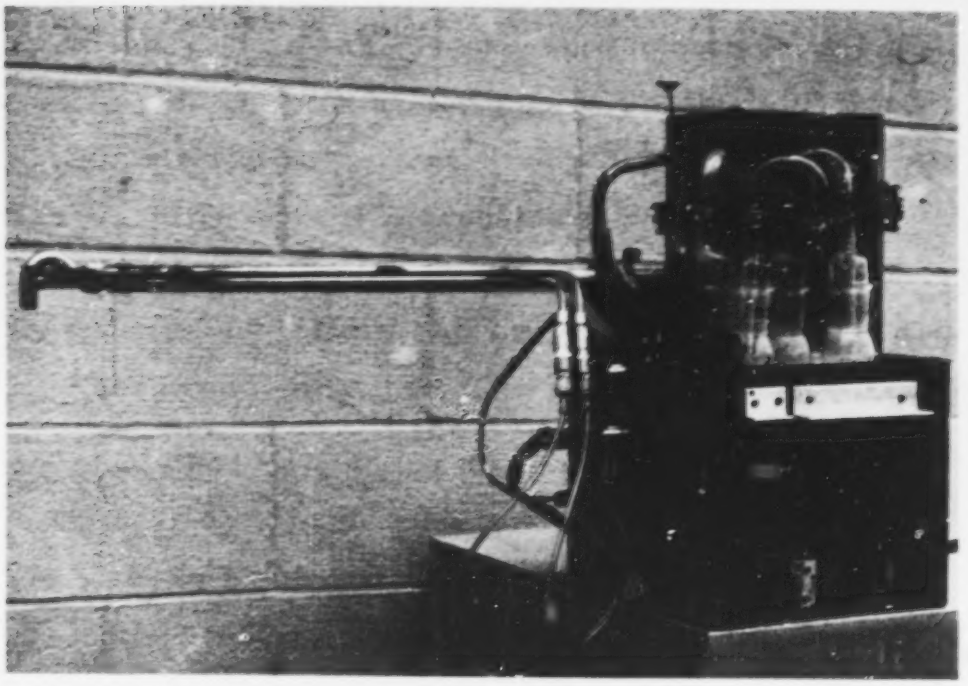


Figure B-2. Phosphoric acid mist sampling train.

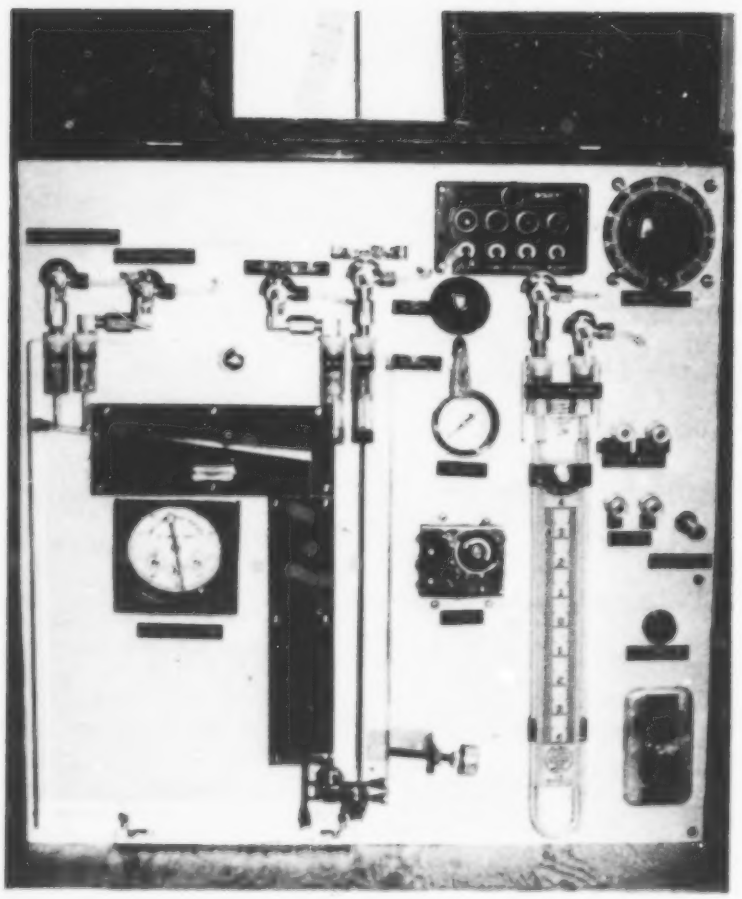


Figure B-3. Control panel of phosphoric acid mist sampling train.

nickel-chromium alloy wire is wrapped with fiber glass tape, and is encased in a 1-inch stainless steel tube. The probe connects to a cyclone (3) and filter (4). The cyclone and filter are housed in an electrically heated box (5), which thermostatically maintains a temperature of 250°F. The cyclone is designed to make a size cut at about 5 microns. When phosphoric acid mist is sampled, the fritted glass and filter paper are removed from the filter housing and all mist smaller than approximately 5 microns is collected in the impingers.

Attached to the heated box is an ice bath (6) containing four Greenburg-Smith impingers connected in series by glass ball joints. The first two impingers are fitted with the standard orifice plate impinger tips while the second two have the orifice tip replaced with 1/2-inch-diameter glass tubes extending to 1/2-inch from the bottom of the flask.

The first impinger (7) receives the stack effluent from the filter. This impinger contains 250 milliliters of deionized water. The second impinger (8) contains 150 milliliters of deionized water. The third impinger (9) is dry, and serves as a knockout pot for entrained water. The fourth impinger (10) contains 175 grams of silica gel, and removes remaining moisture from the gas before it enters the pump and gas meter.

The pump (11), dry gas meter (12), and manometer are housed in a meter box. The gas from the fourth impinger passes through a check valve (14), thermometer (15), pressure gauge (16), vacuum pump (11), dry gas meter (12), dual manometer (13), and calibrated orifice (17). All of these parts are housed in the meter box, and are connected to the impingers by an umbilical cord of rubber tubing to carry the sample gas. Electrical lines, pitot tube, and pressure-sensing tube are also included. This permits a remote location for the meter box and the operator.

Figure B-3 shows the controls on the meter box that include a powerstat for controlling heat to the probe; switches that control the power to the fan, heated box, and pump; and the flow control valves and manometers.

Selection of Sampling Points

The location and number of sampling points are based on size and shape of the duct, uniformity of gas flow in the duct, availability of sampling port, and space required to set up sampling equipment. Straight, vertical ducts that have no flow obstructions for at least 8 diameters upstream and 2 diameters downstream from the sampling point are preferred. For this equipment a 3-inch sample hole is required. In non-cylindrical stacks the traverse should be made across the largest dimension. In horizontal ducts the traverse should always be vertical. The importance of selecting proper sampling point locations is paramount if representative reproducible results are to be obtained.

To insure a representative sample of the stack gas, the duct should be divided into a number of equal areas and samples should be taken at the center of each of these areas. The number of areas depends on the size of the stack. This procedure prevents erroneous results due to stratification of the acid mist in the duct. Bulletin WP-50 of the Western Precipitation Company may prove useful in determining the number of areas.

Thermal-process phosphoric acid plants employ continuous processes and are not, therefore, subject to cyclic emission rates. The major factor in selecting sampling time is the quantity of material collected in the cyclone and impingers. The limiting factor is the moisture content of the stack gas. Sample runs are usually terminated before water entrainment occurs in the third impinger. Optimum time is approximately 1 hour.

Stack Gas Velocity

The pitot tube is used for most velocity measurements. The basic equation for calculating velocity is

$$V_s = 174K \sqrt{HT_s} \times \frac{29.9}{P_s} \times \frac{29.0}{MW}$$

where:

V_s is the gas velocity in feet per minute, K is the pitot tube calibration factor, H is the velocity head in inches of water, T_s is the stack gas

temperature in °R, P_s is the absolute pressure of stack gas in inches of mercury, and MW is the molecular weight of the process gas. This equation simplifies to $V_s = 174\ \sqrt{HT_s}$ when the stack pressure is approximately equal to 29.9 and the molecular weight of the process gas is equal to that of air (29.0).

Sampling Rate Determination

In the use of the acid mist train, a sampling rate of about 1 cfm at 70°F must be maintained in order to insure separation of particles larger than 5 micrometer diameter in the cyclone.

Nozzle area is then determined by dividing sampling rate by stack gas velocity, i.e.,

$$A_n = \frac{Q,\ \text{sampling rate at stack gas conditions}}{V_s,\ \text{stack gas velocity}}$$

If the gas temperature is below the acid dew point at the sampling port, the mist must be sampled isokinetically.

It is, of course, impractical to vary nozzle size when sampling has begun. Therefore, if gas velocity varies considerably, the sampling rate must be varied and either cyclone efficiency or isokinetic sampling must be sacrificed. Isokinetic sampling is not necessary if previous testing has shown that about 90 percent of the acid mist particles are below 3 to 5 micrometers diameter.

Sampling rates and the corresponding orifice pressure drop should be computed for each sampling point before sampling is begun. These values should be recorded on the data sheet (Figure B-4). Care must be taken in using the orifice calibration curve at various temperatures and pressures. A typical orifice calibration curve is shown in Figure B-5. The following equations may prove useful:

$$\Delta P_o = \Delta P\ (\text{calib}) \times \frac{530}{T_o} \times \frac{P_b - P_o}{29.9} \times \frac{MW}{29.0}$$

$$Q_o = Q\ (\text{calib}) \times \frac{T_o}{530} \times \frac{29.9}{P_b - P_o}$$

ΔP_o = pressure drop across orifice at orifice pressure and temperature, in. H_2O

P_b = barometric pressure, in. Hg

ΔP (calib) = pressure drop across orifice at orifice calibration conditions, in. H_2O

T_o = temperature at orifice, °R

P_o = gauge pressure at inlet to orifice, in. Hg

MW = molecular weight of gas

Q_o = flow through orifice at orifice temperature and pressure, cfm

Q (calib) = flow through orifice at calibration conditions, cfm

A sample calculation illustrates the procedure - assume T_o = 100°F, P_o = 2 in. Hg, MW = 29.0, and P_b = 29.9 in. Hg. Desired sampling rate at 70°F is 1 ft^3/min at 100°F (the stack temperature). Stack velocity measured by pitot tube measurements was 1350 ft/min. The sample nozzle area is then equal to $\frac{1.05\ ft^3/min}{1350\ ft/min} = 0.778 \times 10^{-3}\ ft^2$. The area of the probe selected was $0.8 \times 10^{-3}\ ft^2$.

The required flow at the sampling point is the stack velocity times the probe area or 1,350 fpm x 0.8×10^{-3} = 1.08 cfm at stack temperature and pressure.

The corresponding orifice pressure drop at this flow is obtained by (1) entering the orifice calibration chart at the desired gas volume and reading the orifice pressure drop, and (2) converting this pressure drop to conditions under which the orifice will operate, i.e.,

1. Enter chart at 1.08 cfm and read P = 6.5 in. at calibration conditions.
2. $\Delta P_o = 6.5\text{ in.} \times \frac{530}{560} \times \frac{29.9-2.0}{29.9} = 5.74$ in. at orifice conditions.

Desired orifice setting is then 5.74 inches at this sampling point.

Sample Collection

Add distilled or deionized water to the first and second impingers and silica gel to the fourth impinger. Turn heat on probe and cyclone box and allow about 10 minutes until the system maintains a temperature of about 10°F above the stack gas temperature. Use a powerstat

Plant_____
Location_____

Date_____
Test No._____
P_b=_____

		ORIFICE DATA*				METER DATA		
Position	Time, min	Desired flow, cfm $=A_n \times V_s$	ΔP_o, in.H_2O	T_o, °F	P_o, in.Hg	Reading, ft^3 Q_m	P_m, in.Hg	T_m, °F

*At stack conditions.

$$\Delta P_o = \Delta P_{(Calib)} \left(\frac{530}{460+T_o} \times \frac{P_b - P_o}{29.9} \times \frac{MW}{29.0} \right) =$$

$$Q_s = \text{Volume sampled in scf} = Qm \times \frac{530}{460 + T_m} \times \frac{P_b - P_m}{29.9} =$$

	cc of NaOH, N=	mg HNO_3= cc x N x 63	Concentration, mg/ft^3
CYCLONE			
IMPINGERS			
TOTAL			

Figure B-4. Data sheet for sampling phosphoric acid mist.

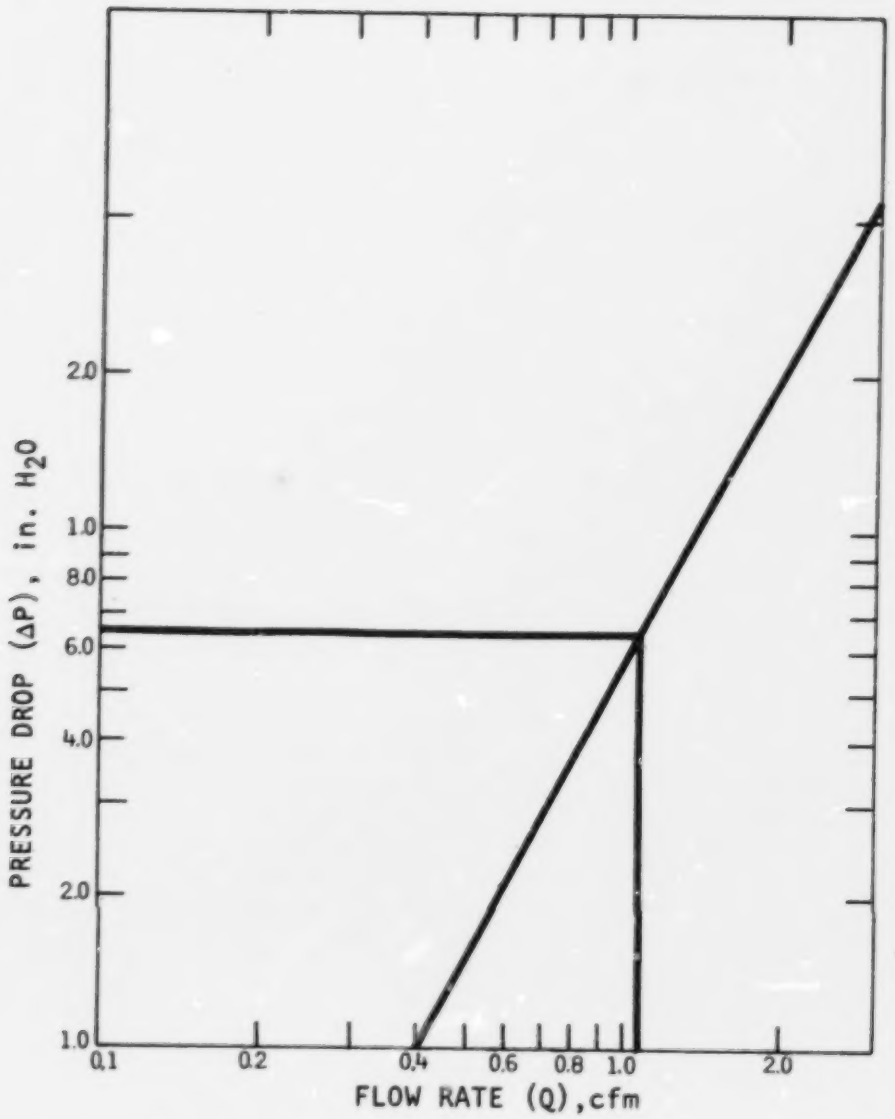


Figure B-5. Typical orifice calibration curve at 70°F and 29.9 in. Hg.

to adjust temperature. Add crushed ice to the impinger water ba .

Pressure check the train by plugging the probe and drawing a vacuum of 20 inches of Hg. Close the line leading from the train; the vacuum should remain at 20 inches Hg if the train is leak proof. Slowly remove the plug from the probe to release vacuum and open the line leading from the train.

When train reaches operating temperatures, sampling can begin. Record all pertinent data during the test. Compute the desired flow and corresponding pressure drop before sampling begins.

. The sampling period will depend on the size of the stack.

Normally a 5-minute sample is withdrawn from each sample area; i.e., eight sample areas will require 40 minutes.

When the sampling is complete, allow the train to cool. Remove sample from probe, cyclone, and connecting tubing by rinsing with distilled water into a suitable sample bottle. The acid mist collected in the impingers should be washed into a second sample bottle.

SAMPLE ANALYSIS (Colorimetric Method)

The ammonium phosphomolybdovanadate colorimetric method used in the analysis of phosphate samples was adopted from standard operating procedures of the U.S. Industrial Chemical Company[15] and the Association of Official Analytical Chemists.[16] This method is based on the spectrophotometric determination of the yellow ammonium phosphomolybdovanadate complex formed when orthophosphate reacts with ammonium molybdate-vanadate reagent in an acid medium. The method is applicable to materials in which phosphorus compounds can be quantitatively oxidized to the orthophosphate form.[17, 18, 19]

Acid hydrolysis (HNO_3-HCl, 6 to 1) is used to destroy any organic material present in the sample and to hydrolyze any phosphate in the meta or pyrophosphate form to orthophosphate. The system obeys Beer's law to about 2 milligrams of phosphorus pentoxide (P_2O_5) per 100 milliliters of solution. Results of analyses are reported in terms of P_2O_5.

Reagents:

All reagents are prepared from ACS analytical reagent-grade chemicals in phosphate-free distilled or deionized water. Reagents that will be used are:

1. Nitric acid (concentrated).
2. Hydrochloric acid (concentrated).
3. Perchloric acid (70%).
4. Ammonium molybdate solution (0.2 M). Dissolve 35.3 grams of ammonium molybdate tetrahydrate $\left[(NH_4)_6\ Mo_7O_{24}\cdot 4H_2O\right]$ in distilled water and dilute to 1 liter. The reagent is stable at room temperature and may be stored in a glass stoppered bottle for at least 3 months.
5. Ammonium vanadate - perchloric acid solution (0.02 M NH_4VO_3 - 4 M $HClO_4$). Dissolve 1.17 grams of ammonium metavanadate in 200 ml of distilled water and transfer to a 500-ml volumetric flask. Acidify with 172 ml of 70% perchloric acid, and dilute with distilled water to 500 ml. This

reagent may be stored at room temperature for several months.

6. Standard phosphate solution. Dry several grams of potassium dihydrogen phosphate (KH_2PO_4) in an oven at 105°C. Dissolve exactly 1.917 grams of dried KH_2PO_4 in distilled water and dilute to 1 liter in a 1-liter volumetric flask. One ml of this solution is equivalent to 1 mg of P_2O_5.

Apparatus:

1. Analytical balance.
2. Volumetric flasks, 100-, 500-, 1000-ml.
3. Erlenmeyer flasks, 250-ml.
4. Hotplate.
5. Spectrophotometer. This instrument should be capable of measuring color intensity at 400 mμ in 0.5-in. absorbance cells or larger.
6. Constant-temperature water bath. (20°C ± 2°C).
7. Filter paper (Whatman No. 42).
8. Filter funnels and rock.
9. Pipettes (1-, 2-, 5-, 10- and 20-ml).

Analysis:

1. Field samples arrive in two sample bottles. Probe and cyclone washings are in one bottle, and impinger solution is in the other. Each field sample is made up to a known volume.

2. Transfer an aliquot of the sample to a 250-ml Erlenmeyer flask. Simultaneously, prepare a blank (distilled water) and treat in the same manner. Digest the sample and blank (distilled water) with 30 ml of nitric acid and 5 ml of hydrochloric acid. Evaporate until HCl fumes are produced (i.e. almost to dryness) on a hotplate.

3. Cool, dilute to 25 ml with distilled water, and filter through Whatman No. 42 filter paper into a 100-ml volumetric flask to remove any insoluble material. Wash filter and flask

several times with 5- to 10-ml portionsof distilled water, and dilute to 100 ml.

4. Pipet 10 ml of the filtrate into another 100-ml volumetric flask.

5. Add 10 ml of ammonium vanadate-perchloric acid solution and 20 ml of ammonium molybdate solution to the 100-ml volumetric flask and dilute to the mark with distilled water.

6. Place the samples in a water bath (20°C). Allow 15 minutes for complete color development.

7. Measure the absorbance against the distilled water-reagent blank, prepared simultaneously, at a wavelength of 400 mμ using a spectrophotometer and 0.5-in. cells.

8. Obtain the number of milligrams of P_2O_5 present from a previously prepared calibration curve, where absorbance was plotted versus milligrams of P_2O_5.

9. If the amount of P_2O_5 in the aliquot of the sample used is greater than 2 mg, estimate the amount of P_2O_5 present by extrapolating the calibration curve and calculate the proper aliquot size needed. Take an aliquot from the prepared filtrate (i.e. the remaining 90 ml) calculated to have an amount of P_2O_5 suitable for quantitative analysis (0.5 to 2 mg), and proceed with the analysis.

Calculation:

$$\text{Total mg } P_2O_5 = \frac{(\text{mg } P_2O_5 \text{ found})\ (\text{volume of original solution})}{\text{aliquot volume}}$$

Preparation of Calibration Curve

1. Pipet exactly 0, 0.5, 1.0, 1.5, and 2.0 ml of standard P_2O_5 solution (1 ml = 1 mg P_2O_5) into 100-ml volumetric flasks.

2. Add the color developing reagents as in step 4 of the analysis and dilute to the 100-ml mark. Place samples in a water bath (20°C) and allow 15 minutes for full color development.

3. Measure the absorbance at 400 mμ.

4. Plot absorbance versus milligrams of P_2O_5 on square grid graph paper. The curve follows Beer's law up to 2 mg of P_2O_5 per 100 ml of solution.

Discussion of Procedure

Precautions:

1. Use proper protective equipment and safety precautions when handling perchloric acid. In case of contact, flush with plenty of water for 15 minutes.
2. Temperature and final acid strength play an important roll in color development and stability. A constant temperature bath (20°C ± 2°C) should be used. Maximum color will develop in 15 minutes; absorbance will remain constant for at least 2 hours.[17] Final acid strength should be constant at 0.4 M $HClO_4$ for each sample and blank. Slight increases in absorbance are encountered when acid molarity is decreased from 0.40 to 0.20.[20]

Interferences:

Certain substances interfere with the ammonium phosphomolybdovanadate color reaction.

1. Certain ions such as ferrous, stannous, hydrazonium, and iodine should be absent because they reduce the color complex to molybdenum blue.
2. Oxalates, tartrates, and citrates complex molybdenum and tend to bleach the color.[17]
3. High concentrations of iron in the sample cause high results; however, the iron salts can be converted to the perchlorate complex ion which absorbs less light.[15]
4. The interference of dichromate is well known and results from the close resemblance of the color of the ion to the yellow complex ammonium phosphomolybdovanadate. If present, the simplest procedure seems to be the volatilization of the undesired chromium as chromic chloride from hot perchloric acid. Perchloric acid may be used as an oxidizer, provided an $HClO_4$ fume hood is available.[17]

Comments:

This method is applicable to the determination of total phosphates in the concentration range of from about 50 μg to 2 mg. The precision encountered when replicate samples were analyzed was ± 1.0 percent.[17] The same reproducibility has been obtained in the laboratory.

SAMPLE ANALYSIS (Acid-Base Titration Method)

The acid-base titration of phosphoric acid in stack gas samples was adapted from the standard assay procedures for phosphoric acid as described in Reagent Chemicals, ACS Specifications (1960).[21] This method is applicable to particulate samples collected from effluents of furnace phosphoric acid plants. An aliquot of the sample is titrated with standard sodium hydroxide to the disodium hydrogen phosphate equivalence point, using thymolphthalein as an indicator. One ml of one normal sodium hydroxide is equivalent to 0.049 gram of phosphoric acid.

Reagents:

All chemicals used must be ACS analytical-reagent grade. Reagents that will be used are:

1. Water. Deionized or distilled water.
2. Thymolphthalein (0.1 percent). Dissolve 0.10 gram of thymolphthalein in 100 ml of ethanol.
3. Sodium hydroxide (1 N). Dissolve 40 grams of sodium hydroxide in 1 liter of deionized or distilled water. Standardize against potassium acid phthalate by using phenophthalein as an indicator.
4. Sodium hydroxide (0.1 N). Dissolve 4.0 grams of sodium hydroxide in 1 liter of deionized or distilled water. Standardize against potassium acid phthalate by using phenophthalein as an indicator.

Apparatus:

1. Absorber. Three Greenburg-Smith impingers or other collection devices capable of removing phosphoric acid mist from stack gases.

2. Buret. Standard 50-ml buret.

3. Flasks. Erlenmeyer (250-ml).

Analysis:

Transfer the sample to a volumetric flask, and dilute to a known volume. Pipet an aliquot of the sample into a 250-ml Erlenmeyer flask. Wash down the sides of the flask with deionized-distilled water, and add 10 to 12 drops of thymolphthalein indicator. Titrate to the light blue endpoint with standard 0.1 N or 1 N sodium hydroxide, whichever is necessary. The strength of sodium hydroxide used will depend on the amount of phosphoric acid present in the aliquot. A reagent blank should also be run with samples.

Calculations:

Calculate the number of grams of phosphoric acid present in the sample by the following formula:

$$H_3PO_4 \text{ (grams)} = (A-B) \times C \times D$$

Where:

A = ml of 0.1 N or 1 N NaOH required in titration

B = ml of 0.1 N or 1 N NaOH required by reagent blank

C = 0.049 gram H_3PO_4 per ml for 1 N NaOH, 0.0049 gram H_3PO_4 per ml for 0.1 N NaOH

$$D = \text{aliquot factor} = \frac{\text{Volume of sample (ml)}}{\text{Volume of aliquot (ml)}}$$

Calculate the parts per million concentration of H_3PO_4 by the following formula.

$$\text{ppm } (H_3PO_4) = \frac{\text{grams } H_3PO_4 \times 24.1 \text{ liters/mole} \times 10^6}{98 \text{ grams/mole} \times V}$$

Where:

$24.1 \frac{\text{liters}}{\text{mole}}$ = gram molecular volume at 70°F

98 = gram molecular weight of H_3PO_4

V = Volume of gas samples (liters)

Discussion of Procedure

In this acid-base titration, phosphoric acid is converted to

disodium hydrogen phosphate (Na_2HPO_4), and the pH at the equivalence point is about 10. The equivalence point of the titration is detected by a color change in the thymolphthalein indicator from colorless to blue. Any other soluble acids or bases collected would interfere in the analysis. This method is suitable, therefore, when only small amounts of other acids or bases are present in the sample.

When this procedure is compared with the ammonium phosphomolybdovanadate colorimetric procedure for phosphates, good agreement is obtained. With standard solutions of phosphoric acid, the results of the titration method are 2.5 percent lower than those obtained with the colorimetric procedure, which is well within experimental error When both the titration and colorimetric procedures are applied to samples collected from effluents of thermal phosphoric acid plants, the results of the titration procedure are within $\pm$ 7.6 percent of those obtained using the colorimetric procedure.

DETERMINATION OF NITROGEN OXIDES IN STACK GAS

(Phenoldisulfonic Acid Method)

The phenoldisulfonic acid method is applicable to the determination of total oxides of nitrogen (nitrous oxides excepted) in stack gases in the concentration range of from 5 to several thousand ppm.[22] Nitrogen oxides are collected in an evacuated flask containing an absorbant consisting of hydrogen peroxide in dilute sulfuric acid and are oxidized to nitric acid. The nitric acid formed is used to nitrate phenoldisulfonic acid, which, when reacted with ammonium hydroxide, forms a yellow compound (5-nitro, 6 hydroxy, 1, 3-benzenedisulfonic acid, triammonium salt). The intensity of the color produced is proportional to the concentration of nitrogen oxides in the sample and is measured spectrophotometrically at 420 mμ.

Inorganic nitrates, nitrites, or organic nitrogen-bearing compounds easily oxidized to nitrates interfere with the method. The method described in this report is an adaptation of Method D1608-60, American Society for Testing Materials.[23]

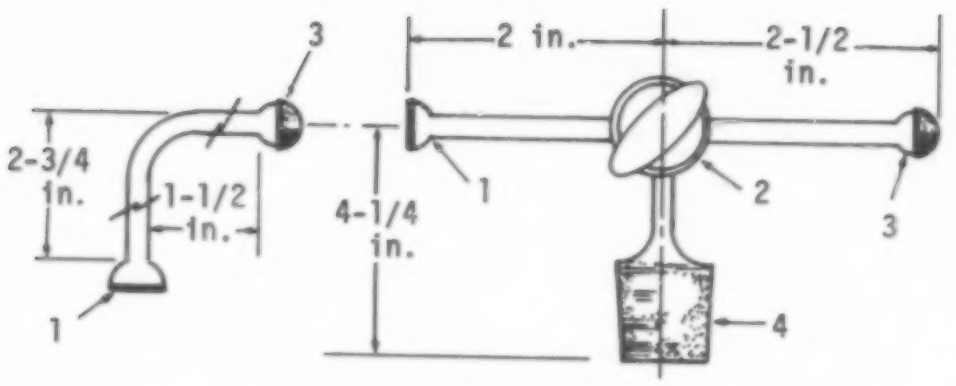
Reagents:

All chemicals used must be of ACS analytical-reagent grade.

1. Water. Distilled or deionized water.
2. Hydrogen peroxide (30 percent). Reagent grade.
3. Hydrogen peroxide (3 percent). Dilute 10 ml of 30 percent H_2O_2 to 100 ml in a 100-ml volumetric flask with water.
4. Sulfuric acid (0.1 N). Dilute 2.8 ml of concentrated H_2SO_4 to 1 liter with water.
5. Absorbing reagent. Dilute 6 ml of 3 percent H_2O_2 to 1 liter with 0.1 N H_2SO_4. This solution is stable and may be used for at least 30 days. Analyses show that the percent H_2O_2 in the absorbing reagent remains constant over a 49-day period.
6. Sodium hydroxide (1N). Dissolve 40 grams of NaOH pellets in water, and dilute to 1 liter.
7. Ammonium hydroxide (concentrated).
8. Sulfuric acid (fuming).
9. Phenoldisulfonic acid solution. Dissolve 25 grams of pure white phenol in 150 ml of concentrated H_2SO_4 on a steam bath. Cool, and add 75 ml fuming sulfuric acid. Heat to 100°C for 2 hours. Store in a dark, stoppered reagent bottle.
10. Potassium nitrate solution (standard). Dissolve 0.5495 gram of KNO_3 in 1 liter of water in a volumetric flask. Dilute 100 ml of this solution to 1 liter in a volumetric flask. One ml of the final solution is equivalent to 0.025 mg NO_2.

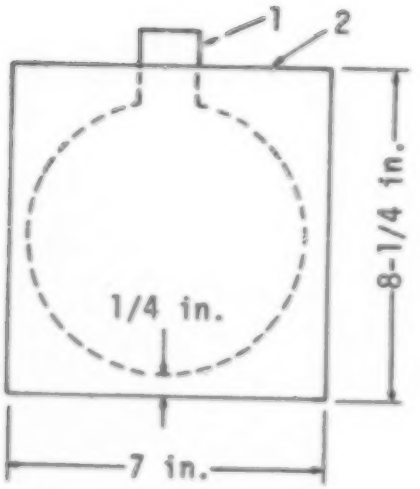
Apparatus:

1. Flasks. Two-liter, Pyrex, round-bottom flask encased in urethane foam with sleeve and accompanying three-way-stop-cock with T-bore should be used. The T-bore has a cone for the verticle leg and balls and sockets for the horizontal legs (see Figures B-6 and B-7).
2. Vacuum system. The vacuum system consists of a vacuum pump capable of pumping 0.1 cfm at 27 in. Hg or more



1. GROUND-GLASS SOCKETS, S NO. 12/5, PYREX.
2. STOPCOCK - THREE-WAY, T-BORE, S, PYREX, 2-mm BORE, 8-mm OD.
3. GROUND-GLASS BALL JOINT, S NO. 12/5.
4. GROUND-GLASS CONES - STANDARD TAPER, S SLEEVE NO. 24/40.

Figure B-6. Three-way stopcock and "L" used to sample stack gases for oxides of nitrogen.



1. BOILING FLASK - 2 LITER, ROUND BOTTOM, SHORT NECK, WITH S SLEEVE NO. 24/40.
2. URETHANE FOAM ENCASEMENT.

Figure B-7. Urethane-encased flask used in sampling stack gases for oxides of nitrogen.

vacuum, connected by a quick disconnect to a vacuum gauge capable of measuring vacuum with an accuracy of 0.25 in. of Hg (see Figure B-8).

3. Thermometer. Dial thermometer, range 25° to 125°F, 5-inch stem.
4. Probe. Pyrex glass tubing (10-mm diameter, 44 in. long). (See Figure B-9.)
5. Glass "L". Connects three-way stopcock to probe (see Figure B-8).
6. Variable transformer. Rated at 7-1/2 amps, 0 to 135 volts.
7. Spectrophotometer. This instrument should be capable of measuring optical density at 420 mμ in 0.5-inch absorbance cells.

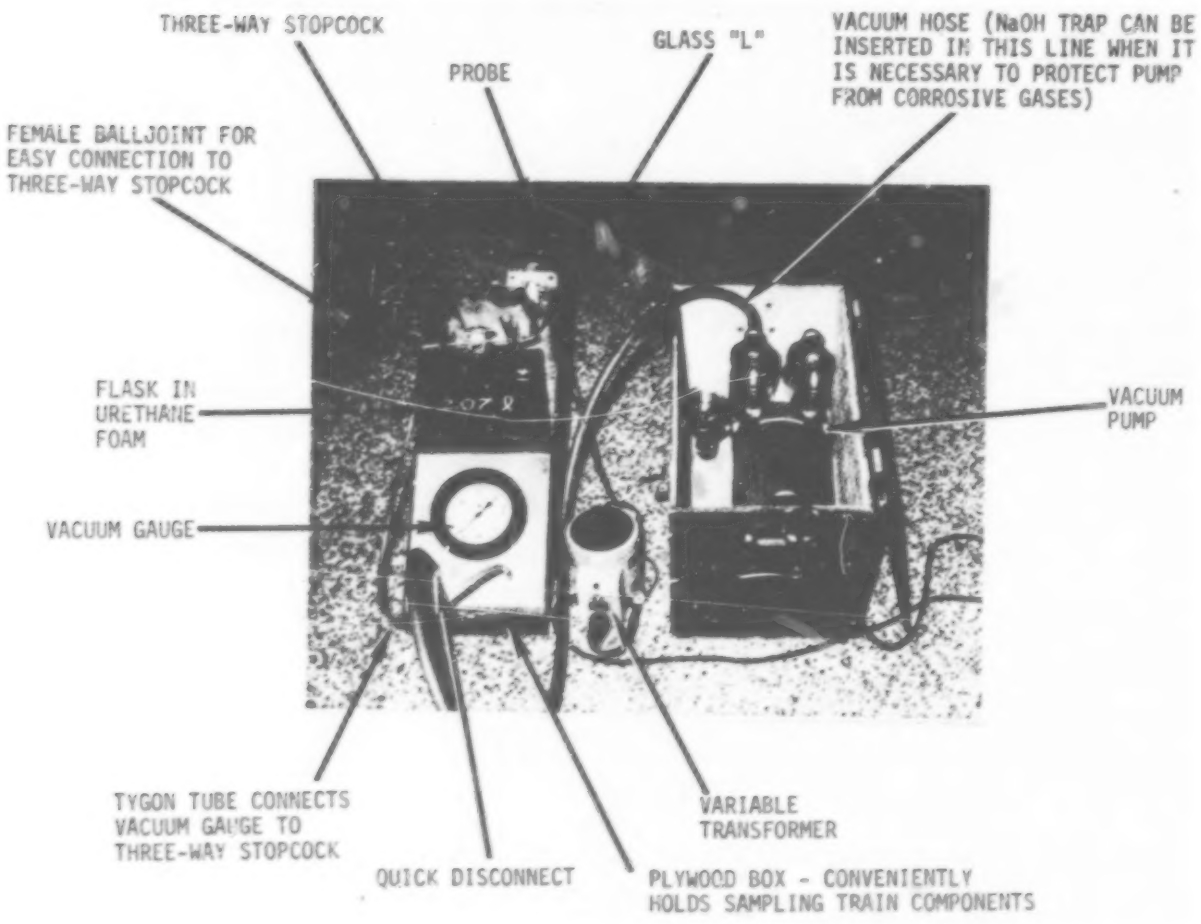

THREE-WAY STOPCOCK
PROBE
GLASS "L"
VACUUM HOSE (NaOH TRAP CAN BE INSERTED IN THIS LINE WHEN IT IS NECESSARY TO PROTECT PUMP FROM CORROSIVE GASES)
FEMALE BALLJOINT FOR EASY CONNECTION TO THREE-WAY STOPCOCK
FLASK IN URETHANE FOAM
VACUUM PUMP
VACUUM GAUGE
TYGON TUBE CONNECTS VACUUM GAUGE TO THREE-WAY STOPCOCK
QUICK DISCONNECT
VARIABLE TRANSFORMER
PLYWOOD BOX - CONVENIENTLY HOLDS SAMPLING TRAIN COMPONENTS

Figure B-8. Apparatus used in sampling stack gases for oxides of nitrogen.

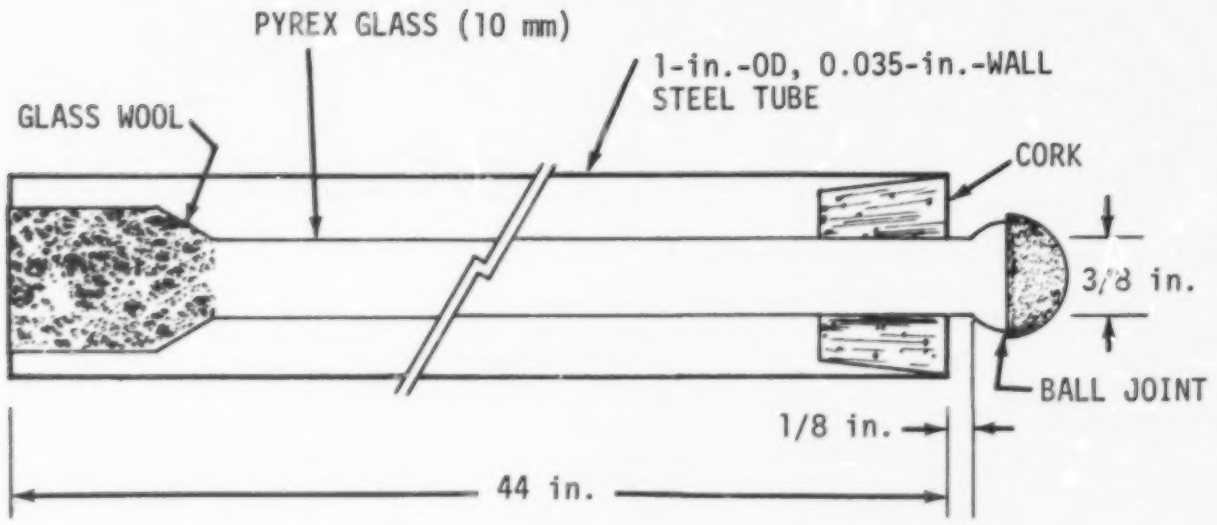


Figure B-9. Sampling probe for oxides of nitrogen.

Sample Collection

Emission sources containing oxides of nitrogen are sampled by a grab sampling technique using an evacuated 2-liter flask. The equipment, developed and used by the Abatement Program, National Air Pollution Control Administration, is shown in Figure B-8.

The following procedure is used for the collection of samples: Add 25 ml of absorbing solution to the flask. Place the three-way stopcock in position on the flask, and insert the stem of the dial thermometer into the urethane foam adjacent to the flask (Figure B-8). Connect the female balljoint of the stopcock to the probe via a glass "L". Insert a wad of glass wool in the intake end of the probe to minimize the amount of particulate matter entering the flask. Connect the male balljoint of the stopcock to the vacuum gauge and pump. Insert the sampling probe into the stack, turn on the pump, and purge the probe and stopcock with stack gas.

If a trap is required to protect the vacuum gauge and pump from corrosive gases, fill a 500-ml plastic bottle with a caustic solution and connect in the line (Figure B-8). If condensation occurs in the stopcock, connect the probe heating element to a variable transformer. Apply sufficient voltage to prevent condensation. Turn the stopcock to connect the vacuum pump and vacuum gauge to the flask. Evacuate the flask to

the vapor pressure of the absorbing solution (approximately 20 mm Hg). Disconnect the vacuum pump line at the quick disconnect, i.e., close the line to the vacuum gauge, and accurately measure the vacuum in the flask. Turn the three-way stopcock to connect the flask to the probe and vacuum gauge. Allow the flask to fill with a sample of stack gas until very little or no vacuum remains; however, avoid pressurizing the flask (a condition that is possible if stack pressure exceeds atmospheric pressure). If the flask takes longer than 15 seconds to fill, the glass wool filter is plugging and should be replaced. Measure the final vacuum in the flask accurately. Position the three-way stopcock so that the flask is closed. Record the flask temperature indicated by the dial thermometer. Disconnect the stopcock at the probe and vacuum source connections. Shake the flask for 15 minutes, and allow to stand overnight to insure complete reaction and absorption of the nitrogen oxides.

Analysis:

Transfer quantitatively the contents of the collection flask to a 250-ml beaker. Wash the flask three times with 10 ml of water, and add to the beaker. For a blank, add 25 ml of absorbing solution and 30 ml of water to a 250-ml beaker. Proceed as follows for both the sample and blank.

Add 1 N NaOH solution to the beaker by drops until the solution is alkaline to litmus paper. Evaporate to dryness on a steam bath, and allow to cool. Add 2 ml of phenoldisulfonic acid solution to the residue, and triturate thoroughly with a glass stirring rod. Make sure all the residue comes in contact with the solution. Add 1 ml H_2O and four drops of concentrated H_2SO_4. Heat the solution on the steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml H_2O, mix well, and add 10 ml of concentrated NH_4OH by drops with constant stirring. Transfer the solution to a 50-ml volumetric flask. Wash the beaker three times with 5-ml portions of water. Dilute to 50 ml, and mix thoroughly. Transfer a portion of the solution to a centrifuge tube, and centrifuge for several minutes. If no

centrifuge is available, the solution may be filtered, provided that the same quality filter paper is used for both samples and blanks.

Determine the absorbance of each sample at 420 mμ using 0.5-inch absorbance cells. If the absorbance is outside the range of the calibration curve, i.e., if absorbance is greater than 0.6, make a suitable dilution of the sample and blank and determine the absorbance. Obtain the number of milligrams of NO_2 present in the sample from a previously prepared calibration curve, where absorbance was plotted versus concentration.

Calculations:

Calculate the concentration of oxides of nitrogen as NO_2 in parts per million by volume as follows:

$$\text{ppm } NO_2 = \frac{(5.24 \times 10^2)\,(C)}{V_S}$$

where:

C = concentration of NO_2, mg

V_S = gas sample volume at 70°F and 29.92 in. Hg, liters

Calculate the volume of gas sampled at standard conditions of 70°F, 29.92 in. Hg.

$$\text{Volume of gas sampled} = \frac{V_f(P_f - P_i) \times 530°R}{T_f \times 29.92 \text{ in. Hg}}$$

Where:

V_f = flask volume, liters

P_f = final flask pressure, in. Hg

P_i = initial flask pressure, in. Hg

T_f = flask temperature, °R

Preparation of Calibration Curve

Pipet exactly 0, 4, 8, 12, 16, and 20 ml of the standard solution containing 0.025 mg NO_2 per ml into 250-ml beakers. Add 25 ml of absorbing reagent to each beaker, and repeat the procedure indicated under analysis of samples. Determine the absorbance at 420 mμ, and plot the absorbance of the solutions versus concentration (mg NO_2).

Discussion of Procedure

This method gives a reproducibility of ± 1 percent when applied to standard samples of inorganic nitrates.[23] When used in motor vehicle exhaust gas analysis, the precision is about ± 5 percent and the overall accuracy is about 3 percent.[24] The precision and accuracy obtained in analysis of stack gas samples should be the same as in the analysis of motor vehicle exhaust gas.

Inorganic nitrates, nitrites, or organic nitrogen compounds that easily oxidize to the nitrate interfere with the test and give high results. Reducing agents such as SO_2, when present in high concentrations, may interfere by reacting with the hydrogen peroxide in the absorbing reagent to leave an insufficient amount for reaction with the nitrogen oxides. Chlorides and halides also tend to interfere, and produce lower results.[23] The continued use of glassware that is etched or becomes etched during the trituration process tends to yield low results and should be avoided.

The color produced is stable for several hours at room temperature (70°F). If the absorbance of the sample is above 0.6, appropriate dilutions of both the sample and blank may be made with water. The absorbing reagent can be prepared in the laboratory and used in the field up to 30 days after its preparation. Reduction of the absorbing reagent in the H_2O_2 concentration was found to be negligible in laboratory experiments conducted over a period of 49 days.

Emission Monitor

Five of the 25 plants from which data are reported use a conductivity cell to monitor the emission of phosphoric acid mist. The system used by the Tennessee Valley Authority is shown in Figure B-10. A small sample stream is withdrawn from the stack by an ejector or a small pump. The acid mist and water are condensed and passed through a conductivity cell before being released to the sewer. A recorder or indicator is attached to the conductivity cell to measure microhms. Model CEL-JDI Industrial Instrument Company* conductivity

*Mention of company or product name does not constitute endorsement by the U.S. Department of Health, Education and Welfare.

cell, or equal, may be used. The recorder is calibrated by stack sampling and can be used to give a continuous reading of the acid mist emissions. Figure B-10 shows that a wet test meter or a calibrated orifice may be used to measure the volume of the sample.

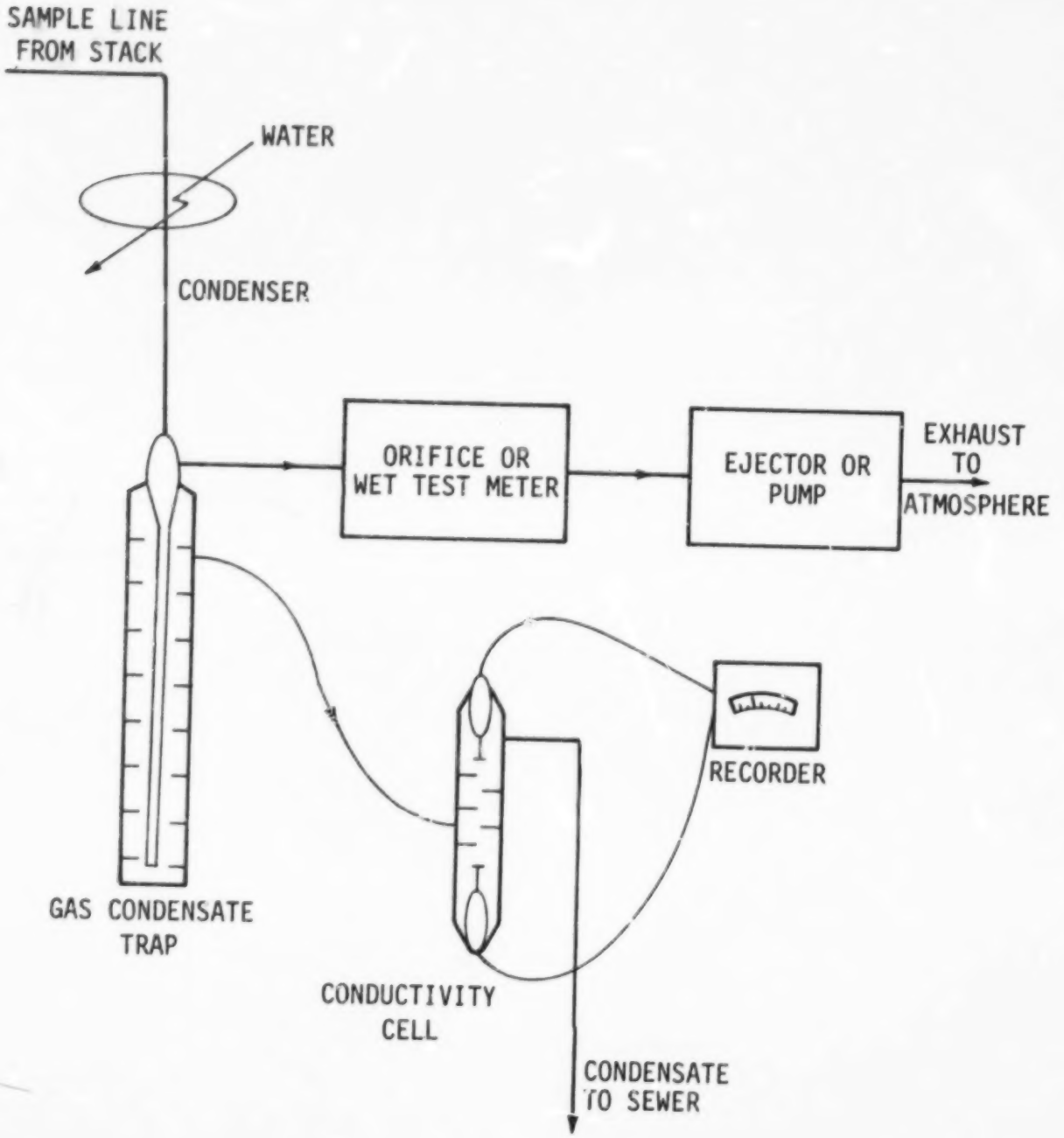


Figure B-10. Diagram of conductivity cell stack monitor.

APPENDIX C: THERMAL-PROCESS PHOSPHORIC ACID ESTABLISHMENTS IN UNITED STATES

The purpose of this tabulation of thermal-process phosphoric acid manufacturing establishments (Table C-1) is to indicate the distribution and principal areas of concentration of this segment of the industry throughout the country.

Listings are without regard to the number of production units at each location. As a result of sale, merger, or lease, company identifications may in some cases differ from those presently in use.

The locations of 30 thermal-process phosphoric acid establishments are shown on the accompanying map (Figure C-1). Three of the establishments shown on the map are not now in operation.

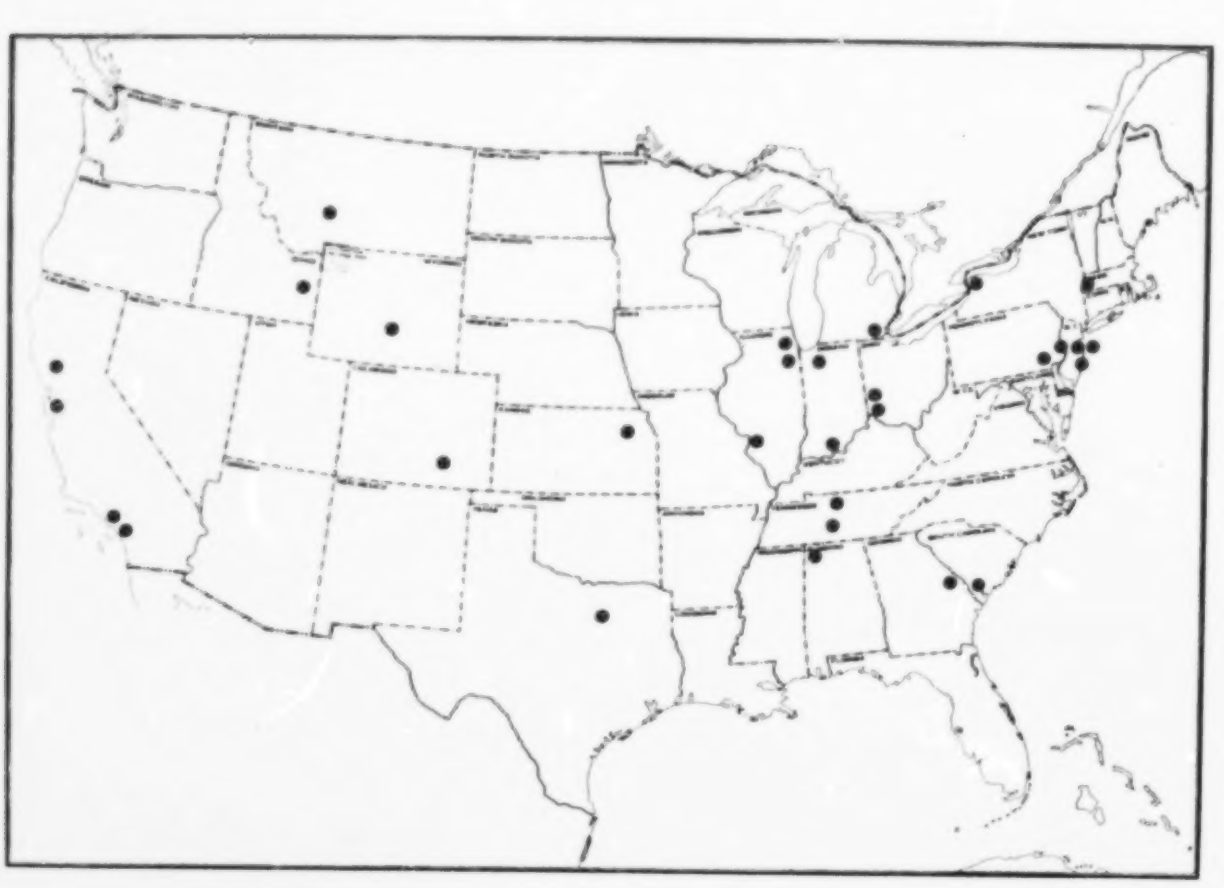


Figure C-1. Location of thermal-process phosphoric acid plants.

Table C-1. THERMAL-PROCESS PHOSPHORIC ACID ESTABLISHMENTS IN UNITED STATES[1,2,25]

State	Company	Location
Alabama	Tennessee Valley Authority	Wilson Dam
California	F M C Corporation	Newark
	Monsanto Company	Long Beach
	Stauffer Chemical Company	Richmond
	Stauffer Chemical Company	South Gate
Colorado	Colorado Fuel and Iron Corporation	Pueblo (not operating)
Georgia	Monsanto Company	Augusta
Idaho	El Paso Natural Gas Company	Georgetown (not operating)
Illinois	Monsanto Company	Sauget
	Stauffer Chemical Company	Chicago Heights
	Stauffer Chemical Company	South Chicago
Indiana	Hooker Chemical Company	Jeffersonville
	Mobil Chemical Company	Gary
Kansas	F M C Corporation	Lawrence
Massachusetts	Hooker Chemical Company	Adams
Michigan	Monsanto Company	Trenton
Montana	Stauffer Chemical Company	Butte
New Jersey	Agrigo Chemical Company	Carteret
	Continental Oil Company	Carteret
	F M C Corporation	Carteret
	Monsanto Company	Kearny
New York	Hooker Chemical Company	Niagara Falls (not operating)
Ohio	Mobil Chemical Company	Fernald
	Monsanto Company	Addyston
Pennsylvania	Stauffer Chemical Company	Morrisville
South Carolina	Mobil Chemical Company	Charleston
Tennessee	Hooker Chemical Company	Columbia
	Stauffer Chemical Company	Nashville
Texas	Hooker Chemical Company	Dallas
Wyoming	F M C Corporation	Green River

APPENDIX D: PHYSICAL DATA

Standard conversions for orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, phosphorus and phosphorus pentoxide are given in Table D-1. Specific gravity and density of phosphoric acid at varying temperatures and concentrations are shown in Figure D-1.

Table D-2 gives process data on gas scrubbing systems of an operating phosphoric acid manufacturing plant. Data on operating conditions during testing and results of tests are given.

Table D-1. CONVERSION TABLES[26]

Name	Formula	Molecular weight	To convert to P_4 multiply by	To convert to P_2O_5 multiply by
Orthophosphoric acid	H_3PO_4	98.14	0.316	0.725
Metaphosphoric acid	$H\ PO_3$	80.05	0.386	0.887
Pyrophosphoric acid	$H_4P_2O_7$	178.11	0.349	0.797
Phosphorus	P_4	124.16	1.000	2.289
Phosphorus pentoxide	P_2O_5	142.16	0.437	1.000
	P_4O_{10}	284.32		

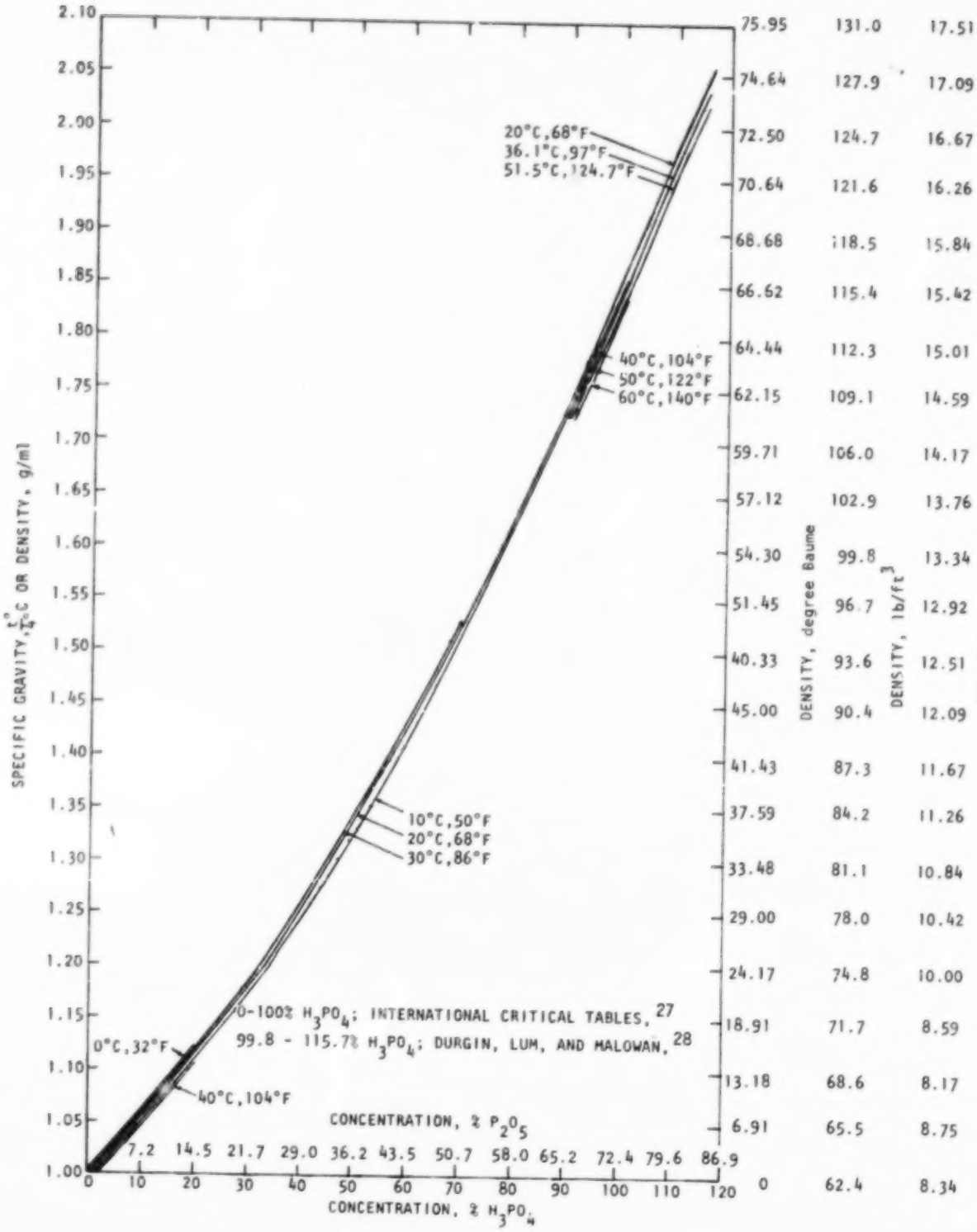


Figure D-1. Specific gravity and density of phosphoric acid. [27,28]

Table D-2. PROCESS DATA ON GAS SCRUBBING SYSTEMS OF TVA NO. 6 PHOSPHORIC ACID UNIT[3]

(Unit produces acid containing P_2O_5 equivalent to 85 to 115 percent H_3PO_4)

Operating conditions						Venturi scrubber									Separator tower								Recovery of P_2O_5		
						Gas entering				Gas			Dilute acid entering			Flows, 1000 lb/hr			Stack gas		Heat removed, 1000 Btu/hr					
Test No.	P_4 feed, lb/hr	Excess air, %	Acid, % H_3PO_4 Product	Acid, % H_3PO_4 Dilute	Cooling water, °F	P_2O_5, lb/hr	Total, 1000 lb/hr	1000 Btu/hr	Temp., °F	ΔP, in. water	Temp., out, °F	Δt, °F	1000 lb	°F	Gas entering, psig	Makeup water	Weak acid	H_2O out in stack gas	Temp., °F	P_2O_5, lb/hr	In jacket water	In stack gas	% of total to plant	lb/hr	% of total to acid unit	Over-all in acid unit, % of total from P_4 feed
Data for 85 to 98 percent H_3PO_4																									
6	2750	42	87.5	38.2	84	2540	26.2	3,530	260	26	139	+2	122	137	2.0	5.10	97	2.01	130	20	710	2,540	10.3	2520	40.0	99.68
10	2920	36	85.7	39.0	85	2760	26.3	4,530	400	32	146	-4	143	150	2.0	5.40	98	2.36	142	2	880	2,990	8.1	2760	41.1	99.98
9	2920	34	86.7	37.6	84	2650	26.4	4,120	315	30	141	-3	143	144	2.0	5.40	97	2.07	136	3	810	2,640	10.2	2650	39.6	99.96
5	3000	42	86.8	42.1	86	2800	26.3	3,430	260	27	140	+2	147	138	2.0	5.10	98	1.91	131	12	800	2,430	9.6	2790	40.6	99.83
3	3130	40	84.9	37.6	86	2940	28.3	3,500	240	37	133	+1	144	132	1.6	6.15	105	2.54	127	7	700	3,120	12.1	2930	40.8	99.50
4	3170	36	87.0	41.9	86	3140	28.8	3,210	250	23	139	+4	148	135	1.6	5.70	107	2.13	128	37	810	2,690	10.3	3100	42.7	99.50
32	3560	40	94.0	45.8	86	3630	33.2	4,790	300	37	138	+1	183	137	1.0	5.75[a]	0	3.00	132	4	620	3,720	9.5	3620	44.5	99.96
33	3650	34	89.7	43.9	86	3420	31.1	3,560	290	2	171	+26	10	145	0.9	5.35	116	3.19	140	26	620	3,980	10.0	3400	40.6	99.69
37	4590[b]	33	98.7	58.8	75	5440	38.7	6,080	480	43	142	-3	206	145	0.9	6.11	135	4.08	137	1	740	5,020	10.3	5440	51.8	99.99
53	5060[b]	23	95.1	47.9	81	5090	41.2	6,730	380	49	147	+2	143	145	0.8	7.45	109	3.43	138	8	740	4,340	8.5	5080	43.9	99.93
50	5083[b]	40	95.8	54.8	79	6440	50.8	9,690	525	51	152	+2	150	150	0.9	8.00	112	4.65	142	1	780	5,880	10.7	6440	55.3	99.99
58	5130[b]	20	95.0	49.0	82	5080	41.0	7,170	450	30	150	+2	150	148	0.9	7.75	107	4.07	141	5	880	5,070	9.7	5070	43.2	99.95
51	5270[b]	40	97.3	53.0	80	6340	50.6	8,820	415	30	157	+9	148	148	0.9	8.00	110	4.38	141	5	820	5,560	10.9	6340	52.5	99.96
48	6050[b]	28	90.2	39.9	62	7430	56.1	12,800	350	35	167	+7	135	160	1.0	13.0	104	7.84	150	8	1400	9,440	14.4	7420	53.6	99.94
59[c]	7060[b]	20	91.7	40.9	84	9720	68.6	19,810	440	53	175	+9	144	166	0.9	20.2	109	12.70	162	30	810	15,120	18.6	9690	59.9	99.81
Data for 105 to 106 percent H_3PO_4																										
1	3800	31	106.3	70.7	78	3290	28.9	2,090	330	<20	137	+7	176	130	1.1	3.60	128	1.67	125	50	830	2,210	7.6	3240	37.2	99.42
2[d]	3960	51	106.3	72.3	78	3240	31.7	2,260	328	<20	141	+7	192	134	2.1	3.60	129	1.41	128	36	890	2,000	7.2	3210	35.4	99.61
41	4040[b]	41	105.3	74.4	45	5320	36.6	3,540	400	53	141	-3	153	144	0.9	4.01	133	1.49	132	2	1730	2,140	8.1	5320	57.6	99.98
40	4330[b]	20	105.9	70.0	57	4860	32.6	3,190	370	30	137	-1	142	138	0.9	4.16	123	1.68	126	5	1100	2,240	7.2	4850	49.0	99.95
31	4330[b]	23	105.9	73.3	82	2970	30.1	3,040	440	53	137	-7	120	144	0.8	4.00	149	1.79	137	2	840	2,440	7.0	2970	30.0	99.98
62	4880[b]	38	106.0	69.7	56	5780	41.0	4,330	370	53	142	-3	183	145	0.9	4.81	127	1.99	135	3	830	2,770	6.7	5780	51.7	99.98
Data for 109 to 112 percent H_3PO_4																										
16	1530	53	109.9	75.9	84	1300	16.6	1,070	270	32	133	-1	192	134	2.0	1.50	125	0.49	126	16	620	780	7.0	1280	36.8	99.55
13	2450	53	110.8	78.2	85	2240	23.7	1,800	330	34	142	-3	159	145	2.0	2.25	125	0.69	137	9	640	1,150	5.9	2230	39.7	99.83
14	2600	54	110.8	79.1	84	2510	24.0	2,050	350	40	145	0	160	145	2.0	2.00	88	0.82	140	11	710	1,300	6.5	2500	42.1	99.82
11	2730	26	109.4	80.9	84	2370	23.5	1,660	330	30	147	+2	201	145	2.0	1.65	128	0.60	135	4	560	1,030	4.6	2360	37.9	99.94
12	2780	40	110.5	82.5	85	2430	23.2	1,890	370	31	156	-2	198	158	2.2	2.10	130	0.65	149	9	760	1,150	6.0	2420	38.0	99.86
7	2910	37	110.8	79.0	84	2720	23.7	1,880	330	30	142	+2	201	140	2.0	1.50	126	0.78	135	13	690	1,220	5.8	2710	40.6	99.80
8	3000	33	111.0	80.6	85	2590	23.1	2,260	430	30	161	+2	203	159	2.0	2.25	127	0.85	147	15	620	1,360	5.6	2580	37.5	99.78
17	3040	38	111.0	79.1	84	2740	22.3	1,750	340	45	143	-1	134	144	2.0	2.25	131	0.64	136	6	1010	1,050	6.4	2730	39.3	99.51
15	3080	34	111.2	75.1	83	2340	23.2	1,940	360	32	141	+2	156	139	2.0	2.25	39	0.90	130	9	790	1,320	6.0	2340	33.2	99.88
18	3560[b]	29	110.5	84.4	82	3510	24.3	1,840	340	25	151	-3	217	154	1.1	2.25	137	0.84	144	15	670	1,330	5.3	3500	42.8	99.81

Table D-2 (continued). PROCESS DATA ON GAS SCRUBBING SYSTEMS OF TVA NO. 6 PHOSPHORIC ACID UNIT[3]

(Unit produces acid containing P_2O_5 equivalent to 85 to 115 percent H_3PO_4)

Test No.	Operating conditions: P_4 feed, lb/hr	Excess air, %	Acid, % H_3PO_4: Product	Acid, % H_3PO_4: Dilute	Cooling water, °F	Venturi scrubber: Gas entering: P_2O_5, lb/hr	Gas entering: Total, 1000 lb/hr	Gas entering: 1000 Btu/hr	Gas entering: Temp, °F	Gas: ΔP, in. water	Gas: temp. out, °F	Gas: Δt, °F	Dilute acid entering: 1000 lb	Dilute acid entering: °F	Separator tower: Gas entering, psig	Flows, 386 lb/hr: Makeup water	Flows, 386 lb/hr: Weak acid	Flows, 386 lb/hr: H_2O out in stack gas	Stack gas: Temp, °F	Stack gas: P_2O_5, lb/hr	Heat removed, 1000 Btu/hr: In jacket water	Heat removed, 1000 Btu/hr: In stack gas	Heat removed, 1000 Btu/hr: % of total to plant	Recovery of P_2O_5: lb/hr	Recovery of P_2O_5: % of total to acid unit	Recovery of P_2O_5: Over-all in acid unit, % of total from P_4 feed
Data for 109 to 112 percent H_3PO_4 (continued)																											
25	3840	+ 16	109.7	76.6	54	3700	27.1	3,240	500	39	149	-4	148	153	0.8	3.01	127	1.92	136	8	1160	2,510	7.8	3690	44.4	99.91
26	3700	- 27	110.6	79.5	58	3980	29.4	3,710	530	38	157	-6	150	163	0.8	3.51	130	2.21	145	4	800	2,930	8.5	3970	46.8	99.96
24	3720	16	111.3	74.3	55	3330	25.9	2,53[illegible]	395	35	140	0	148	140	0.8	2.51	124	1.73	131	13	910	2,260	6.8	3310	38.9	99.85
19	3773[b]	20	111.6	82.8	78	3640	25.9	2,080	360	37	155	-2	200	157	1.1	2.55	137	1.05	144	7	1300	1,590	6.7	3630	42.1	99.82
57	3860[b]	32	109.2	83.1	82	4750	32.2	3,090	400	40	154	-2	188	156	0.7	3.20	137	1.41	148	2	650	2,110	6.1	4750	53.7	99.98
27	4060	[illegible]	110.3	67.6	58	3150	25.9	2,690	410	35	137	-1	140	138	0.8	3.21	120	1.74	122	6	700	2,220	6.3	3150	33.8	99.94
22	4200[b]	26	111.2	85	64	4370	30.8	3,080	433	34	171	0	210	171	1.1	2.55	138	1.17	157	6	1260	1,890	7.6	4360	45.3	99.94
34	4210[b]	40	111.7	94.7	85	3640	35.0	3,570	450	51	199	-3	249	202	0.8	2.00	166	0.88	187	8	950	1,940	5.8	3450	35.8	99.92
36	4340[b]	21	111.8	87.3	83	3340	29.3	2,670	405	48	170	-5	238	175	0.9	2.75	139	0.84	164	2	1080	1,570	4.9	3340	33.6	99.98
54	4470[b]	48	109.3	85.2	81	6450	44.1	5,850	520	40	172	-4	185	176	0.9	4.30	137	2.35	164	4	760	3,500	8.4	6440	64.9	99.97
55	4490[b]	32	110.0	84.8	81	5900	39.2	4,750	480	61	168	-3	189	171	0.8	3.80	136	1.83	161	3	880	2,800	6.8	5900	57.4	99.97
52	4540[b]	32	109.3	82.4	80	5640	38.2	4,510	470	25	171	+3	179	168	0.8	4.00	137	1.83	160	6	860	2,770	6.9	5630	54.2	99.94
61	4560[b]	10	109.6	77.5	83	4760	31.3	3,760	465	39	147	-9	181	156	0.8	3.90	134	1.35	147	4	610	2,010	4.8	4750	45.5	99.96
39	4660[b]	30	109.6	82.0	75	5180	37.5	4,760	530	41	167	-3	230	170	0.6	4.26	153	3.13	160	7	950	4,200	8.9	5170	48.4	99.93
58	4720[b]	32	109.2	87.5	82	5570	39.9	4,850	510	40	178	-5	194	183	0.3	4.00	142	1.96	172	4	860	3,050	7.4	5570	51.5	99.97
38	4790[b]	31	109.4	80.9	73	5060	37.9	5,220	570	39	165	-4	228	169	1.0	4.51	152	3.46	158	6	940	4,560	9.3	5050	46.0	99.95
45	4790[b]	40	110.6	85.1	50	5560	42.3	5,360	550	30	185	+13	199	171	0.9	3.51	142	2.28	160	7	1350	3,370	8.7	5560	50.7	99.94
44	4910[b]	40	110.0	81.9	48	6060	43.7	4,780	465	51	166	-2	191	168	0.8	3.86	138	2.61	152	5	1360	3,680	9.1	6060	53.9	99.96
28	5020[b]	39	110.4	81.8	67	4950	39.1	4,600	500	54	162	-6	150	168	0.8	4.26	161	2.34	154	2	860	3,220	7.4	4950	43.0	99.99
46	5070[b]	20	110.0	80.0	50	5310	38.7	4,270	470	30	154	-4	189	158	0.9	3.81	135	2.10	142	11	1030	2,940	6.7	5300	45.6	99.91
42	5190[b]	21	109.8	78.1	46	5460	37.4	4,670	520	48	156	-2	184	158	0.8	4.21	132	2.27	145	3	1250	3,120	7.6	5450	45.9	99.98
43	5300[b]	25	109.3	76.3	47	6020	42.4	5,340	500	40	158	-4	180	162	0.9	4.51[a]	0	2.52	146	6	1420	3,500	8.1	6010	49.5	99.95
49	5370[b]	30	109.9	79.7	65	6640	45.0	6,170	520	40	163	-3	175	170	0.8	5.31	127	3.05	158	4	1150	4,220	8.6	6630	53.9	99.97
29	5540[b]	16	111.5	82.5	70	6240	39.3	5,910	610	56	185	-7	148	192	0.8	4.51	180	2.73	176	2	760	3,930	7.3	6240	49.2	99.97
60	5540[b]	21	109.9	78.8	82	6760	43.3	6,300	530	50	161	-4	182	169	0.9	5.30	134	2.76	159	7	740	3,880	6.9	6750	53.2	99.95
47	6000[b]	20	110.6	78.0	58	7090	46.1	6,650	550	51	168	-4	179	172	0.8	5.86	128	3.43	157	3	1900	4,650	9.9	7090	51.6	99.98
30	6280[b]	15	111.9	81.0	73	6950	42.1	6,980	615	44	172	-6	144	178	0.8	5.61	161	3.03	165	4	1320	4,200	8.4	6950	48.3	99.97
Data for 113 to 115 percent H_3PO_4																										
20	3390[b]	19	113.2	86.0	78	3360	21.9	1,710	340	35	156	-2	204	158	1.1	2.25	140	0.88	143	14	1210	1,340	7.2	3350	43.5	99.83
23	3690[b]	37	115.0	90.5	64	4190	30.1	3,450	493	35	189	0	221	189	1.1	2.50	149	1.36	171	7	1430	2,190	9.6	4190	49.6	99.91
35	4380[b]	40	113.1	91.7	86	4540	35.9	3,540	433	32	192	+4	245	188	0.9	2.50	163	0.95	173	32	830	1,890	6.2	4500	44.9	99.68
21	4580[b]	24	114.1	85.5	68	4990	31.7	2,890	400	30	158	-1	206	159	1.1	2.50	135	1.26	145	14	1280	1,920	6.8	4980	47.5	99.87

[a] To weak acid receiver.

[b] Two combustion chambers in operation.

[c] Before test No. 59 was made, the 1-1/2-inch carbon intalox saddle packing was removed from the separator tower.

[d] After test No. 2 was made, a damper, or sliding gate, was installed at the throat of the venturi scrubber in order to permit control of gas pressure differential across the venturi.

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